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First-principles study of hydrogen adsorption and permeation in reconstructed cubic erbium oxide surfaces

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HIGHLIGHTS

- The energetics of atomic H on cubic Er_2O_3 surface are studied using DFT+U calculations, as well as the equilibrium sites at the Er_2O_3 surfaces.
- The surface ability depends on the ratio of Er:O for cubic Er_2O_3 surfaces.
- The probability of an H atom penetrating from the surfaces to the bulk site is predicted to be considerable at 873 K or higher temperature.

ARTICLE INFO

ABSTRACT

Understanding surface properties of Er_2O_3, especially in relation to adsorption and permeation of atomic hydrogen, is of considerable importance to the study of tritium permeation barriers. In this work, hydrogen diffusion pathways through the low-index (1 0 0), (1 1 0), and (1 1 1) surfaces of cubic Er_2O_3 have been calculated using density functional theory within the GGA (PBE)+U approach. The dependence of the effective U parameter on lattice constants, bulk moduli, and formation energies of Er_2O_3 has been investigated in detail. The energetics of hydrogen penetration from the surfaces to the solution site in bulk Er_2O_3 were defined using the optimum effective U value of 5.5 eV. For a low surface coverage of hydrogen (0.89×10^{14} H/cm^2), a penetration energy of at least 1.7 eV was found for all the low-index erbium oxide surfaces considered. The results of the present study will provide useful guidance for future studies on modeling defects, such as grain boundaries and vacancies, in tritium permeation barriers.

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1. Introduction

In deuterium–tritium (D–T) fusion reactors, it is anticipated that the tritium/hydrogen barrier will play a critical role in containing and handling hydrogen isotopes within the reactor building and controlling hydrogen isotope release to the environment without incurring exorbitant costs [1,2]. Regarding barrier materials, erbium oxide (Er_2O_3) has attracted much attention for tritium permeation barrier (TPB) applications due to its high permeation reduction factor (PRF), good compatibility with static and natural convection liquid lithium, high thermodynamic stability at high temperatures and in air, and high electrical resistivity [3–7]. Er_2O_3 has recently emerged as one of the most promising materials for use in TPB coatings for the D–T fuelling cycle in fusion blanket systems [8,9]. One of the main justifications for using Er_2O_3 as a TPB coating is the high PRF of Er_2O_3 for hydrogen isotopes, as compared to iron-based materials [10]. It is, therefore, essential to understand

the interaction between atomic hydrogen and erbium oxide for the development of fusion reactors, especially in relation to the adsorption and permeation of hydrogen isotopes in cubic Er_2O_3 surfaces, which is a very important work that remains largely unstudied [11,12].

Interest in the adsorption and permeation of hydrogen isotopes in cubic Er_2O_3 surfaces stems mainly from its relevance to TPB coatings. In the present study, we choose to consider the low-index (1 0 0), (1 1 0), and (1 1 1) surfaces of cubic Er_2O_3 because they have been examined by means of X-ray diffraction (XRD) [4,11,13]. The study of hydrogen adsorption and permeation (or penetration) in the low-index (1 0 0), (1 1 0), and (1 1 1) surfaces is crucial.

Calculations of H penetration in the low-index (1 0 0), (1 1 0), and (1 1 1) surfaces of cubic Er_2O_3 have been carried out by density functional theory (DFT) and the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA–PBE) formalism [14,15]. Because Er_2O_3 is one of the lanthanide oxides, a proper description of the 4f electrons at moderate computational cost is of great importance for the correct prediction of the electronic and magnetic properties of Er_2O_3 [16–18]. The semi-core 4f level of Er_2O_3 has therefore been included in the study of H penetration of Er_2O_3

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surfaces. As reported in Refs. [19–21], the 4f electrons can be well treated by adding an empirical or effective parameter U_{eff} for the 4f orbitals within the GGA + U approach, in which U_{eff} is the sum of the Hubbard potential U, representing the strength between on-site two-electron (Coulomb) interaction, and the parameter $-J$ that adjusts the strength of the exchange interaction. In general, the introduction of the effective parameter U_{eff} leads to a drastic improvement in the description of reduced lanthanide oxides such as Ce_2O_3 [22–24] because GGA + U corrections act to reduce the electron potential locally for the specified orbitals of the respective atoms, e.g., Ce 4f orbitals. As a result, this GGA + U approach reduces the hybridization with orbitals of ligands, e.g., O atoms, in which the underestimation of the intraband Coulomb interaction is corrected via the Hubbard U parameter [19–21]. At present, the systematic study of the optimal U_{eff} parameter in GGA + U corrections for Er_2O_3 is lacking. Therefore, the dependence of the optimal U_{eff} parameter on the lattice constant, bulk modulus, and formation enthalpy has been investigated for a significant improvement of Er_2O_3 properties regarding H penetration from the cubic Er_2O_3 surfaces.

The organization of this report is as follows: in Section 2, we describe the theoretical details used in this study. The results of the dependence of lattice constants, bulk moduli, and formation energies of Er_2O_3 on the U_{eff} parameter, the surface energy of cubic Er_2O_3 (1 0 0), (1 1 0), and (1 1 1) surfaces, and H penetration through these cubic Er_2O_3 surfaces, derived by a consideration of the interstitial H positions on these surfaces, H solution positions in bulk Er_2O_3, and the penetration energies are given in Section 3. Finally, we summarize the main findings of this work in Section 4.

2. Theoretical methods

All calculations have been performed using DFT as implemented in the Vienna *ab initio* Simulation Package (VASP) [25–27]. The electron wave functions were described using the full-potential frozen-core all-electron projected augmented wave (PAW) method within the GGA–PBE formalism [14,15]. The PBE form of the GGA exchange-correlation potential has been used together with the GGA + U variant, as implemented in VASP [28], in which the effective U_{eff} parameter has been studied regarding to lattice constants, bulk moduli, and formation energies of Er_2O_3. Plane waves have been included up to an energetic cutoff of 500.0 eV for all DFT calculations wherein increasing the cutoff resulted in variations of <2 meV/atom (0.192 kJ mol^{-1} atom^{-1}) in the total energy. The sampling of the Brillouin zone has been performed using a Monkhorst-pack scheme [29] with k-meshes of $4 \times 4 \times 1$ for (1×1) surface unit cells of (1 0 0), (1 1 0), and (1 1 1) surfaces of cubic Er_2O_3. 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. Use of the above k-meshes has been verified to be converged to <1 meV/atom (0.096 kJ mol^{-1} atom^{-1}). Atomic relaxations were performed using a conjugate gradient algorithm [30] and the forces on each atom converged to less than 1 meV/nm (0.096 kJ mol^{-1}/nm).

Defect free (1 0 0), (1 1 0), and (1 1 1) surfaces of cubic Er_2O_3 were constructed by the aid of a slab model repeated periodically in all three dimensions and are composed of four stoichiometric Er_2O_3 layers, two relaxed and two unrelaxed, and a vacuum region. A stoichiometric layer consists of one or three Er layers (8 Er atoms) and three O layers (12 O atoms). A vacuum region width between the slabs of 1.4 nm was found to be sufficient to isolate the Er_2O_3 slab from its periodic images. During the optimization, both the adsorbate (H) and the Er and O atoms in the top two stoichiometric layers of the slab were allowed to relax while the remaining Er and O atoms of the slab were frozen in their bulk optimized configurations. The surface energy converged to within 0.01 J/m^2 using

the above tested kinetic energy cutoff of 500.0 eV and k-meshes of $4 \times 4 \times 1$. A single H atom on the as constructed surface layer yields a surface coverage of ~0.89 × 10^{14} H/cm^2.

For the case of surface adsorption, we have analyzed the bonding at several different high-symmetry adsorption sites, i.e., the four-fold hollow and twofold bridge sites (Fig. 2), and conducted DFT calculations on the cubic Er_2O_3 (0 0 1), (1 1 0), and (1 1 1) surfaces. As for asymmetric adsorption on a single side of the slab, dipole corrections originally introduced by Neugebauer and Scheffler [31] have been included in order to correct the errors introduced by the use of periodic boundary conditions. Consequently, the adsorption energy $(E_{ads})_d$ of adsorbate H on different Er_2O_3 surfaces can be calculated as [32,33]:

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

where $E(S)_{H \to d}$ refers to the energy of the system when the H atom is a 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 one-half of the molecular hydrogen energy. H penetration from the surface to the solute site has been calculated using the climbing image nudged elastic band (CINEB) method [34], as implemented in the DFT calculations.

Consideration of quantum effects [35] is important at low temperature for light species such as H. Therefore, zero-point-energy (ZPE) corrections have been calculated by summing up the zero-point vibrational energies of the H atom's normal mode, i.e., $ZPE = 1/2 \sum h\nu_i$, where ν_i is the real normal mode frequency [35,36].

3. Results and discussions

3.1. Dependence on U

At room temperature, Er_2O_3 is an insulator featuring a cubic $Ia3$ structure with the experimentally determined lattice parameter $a_0 \approx 1.055$ nm and bulk modulus $B_0 = 140.7/180.3$ GPa [12,37,38], in which a_0 was determined by X-ray diffraction, and B_0 was calculated via resonance ultrasound spectroscopy (RUS). In addition, the experimental formation energy E_f of Er_2O_3 is 19.0 eV [42], which was measured in hydrochloric acid of various concentrations using a calorimeter interfaced with a computer and an interactive set of computer programs. The dependence of the parameter U_{eff} on lattice constants, bulk moduli, and formation/cohesive energies is given in Fig. 1. The present lattice constants and bulk moduli have been obtained from the corresponding energy minimization at constant volume and by fitting a Birch–Murnaghan 3rd-order equation of state (EOS) to the resulting energy–volume data [39,40]. In addition, the formation/cohesive energy per Er_2O_3 unit for the cubic unit cell has been calculated using the following formula:

$$E_f = E(Er_2O_3) - 2E(Er) - 3E(O), \qquad (2)$$

where $E(Er_2O_3)$ is the energy of bulk Er_2O_3 per formula unit (f.u.), $E(Er)$ is the energy per atom of metallic Er or the cohesive energy of metallic Er, and $E(O)$ is the energy per atom of molecular O_2.

Most of the conducted GGA + U calculations, although performed using different effective parameters U_{eff}, accurately predicted the experimental lattice parameter a_0, the experimental bulk modulus B_0, and the experimental formation/cohesive energy E_f. Overall, the lattice constant is predicted to be somewhat longer than a_0, while the bulk modulus is predicted to be somewhat smaller than B_0, which gives a slightly less accurate description of the atomic structure of cubic Er_2O_3. The deviation observed between the experimental and calculated values for Er_2O_3 is similar to that observed for other lanthanide oxides such as Ce_2O_3 and CeO_2 [41]. The structural data and formation/cohesive energy result of Er_2O_3 given in Table 1 seem to be only modestly influenced by the value of