First-Principles Study of the Hydrogen Resistance Mechanism of PuO₂

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1. INTRODUCTION

Plutonium (Pu) is one of the strategically important materials in nuclear explosives and nuclear energy supply. Pu-Śf electrons just lie on the turning point of delocalization to localization in the actinide series.1–4 This peculiarity of Pu-Śf electrons is sensitive to the physical or chemical environments and results in many anomalous properties, among which high chemical reactivity is the most prominent one.5 Thus, the surface oxidation of Pu is unavoidable during its long-term storage, handling, or preparation.6 As is known, the sandwich structure of PuO₂/α-Pu₂O₃/Pu is one reasonable approximate model for the surface oxidation state of Pu in air.5,6,7 Recently, Ao et al. theoretically explored the detailed model of Pu-oxide overlayer and established a ladder-like ultrathin transition layer in the chemical formula of Pu₆O₁₅₋ₓ between PuO₂ and α-Pu₂O₃.8 The hydriding corrosion of Pu is catalytic in the presence of oxygen and finally cause the pyrophoricity of Pu.5,6 The hydriding process of oxide-coated Pu follows the detailed model of Pu-oxide overlayer and can be divided into four periods:9–11 induction, nucleation or acceleration, bulk hydriding, and termination. The induction period mainly stems from hydrogen diffusion through Pu-oxide overlayers and can usually be divided into (i) H₂ physisorption and dissociative chemisorption on Pu-oxide surface; (ii) H penetration into Pu-oxide subsurface; (iii) H diffusion and dissolution in PuO₂/α-Pu₂O₃ overlayers; (iv) H transfer across α-Pu₂O₃/Pu interface; (v) H dissolution and diffusion in Pu matrix; and (vi) H accumulation to saturation and preliminary Pu-hydride nucleation.10,12

Since hydrogen reacts violently with Pu metal, above-mentioned steps (i), (ii), and (iii) involved interactions between hydrogen and Pu-oxide overlayers can be the rate-limiting steps of Pu-hydriding process.5,13,14 Hence, many experimental and theoretical works have been devoted to investigating the roles of Pu-oxide overlayers and the corresponding influencing factors in the Pu hydriding process. Haschke et al. investigated the different roles of PuO₂ and α-Pu₂O₃ in the Pu-hydriding process, and they concluded that the PuO₂ outer layer can effectively resist a hydrogen attack.5 Dinh et al. concluded that the α-Pu₂O₃ interlayer cannot effectively resist a hydrogen attack but provides main hydrogen nucleation sites.14 According to the experiments, they further predicted that the solubility of hydrogen in PuO₂ is orders of magnitude lower than the required nucleation solubility for Pu–H reaction, thus, intact PuO₂ acts as a protective screen against Pu-hydriding.14,16 Based on the PuO₂-covered Pu,
McGillivray et al. further investigated the hydrogen-pressure-dependent hydriding induction time and nucleation rate.9

Because of the radioactivity, the toxicity of Pu, and the complexity of Pu-oxide, experiments have not provided an in-depth understanding of the hydrogen behaviors in the Pu-oxide overlayers. Thus, the primary hydrogen resistance mechanism of PuO2 has not been clarified; namely, it is unclear whether it is mainly a surface-reaction-limited, or bulk-diffusion-limited, or the bulk-solvability-limited mechanism, or the combination of all the above. Our previous work revealed that the collision-induced dissociation barriers of H2 on intact and defective PuO2(111) surface are 3.20 and 2.00 eV, respectively.17 Only then can H penetrate into the close-grained PuO2(111) film with a high barrier of about 4.00 eV.17 Yu et al. showed that the dissociation barrier of H2 is 0.48 eV on the open PuO2(110) surface with Pu cations exposed, while their further investigations found that H migration from the PuO2(110) surface to the subsurface is also difficult with a barrier of 2.15 eV.16,19 These results demonstrate that an intact PuO2 layer can suppress the H2 dissociation and H penetration into the subsurface; on the contrary, the micropictures of H2 dissociation and migration on an ideal α-PuO2(111) surface are quite different.17 The penetration and migration barriers of H2 in α-PuO2 are much lower than the collision—dissociation barrier of H2 on the intact PuO2(111) surface,17 which directly proves that α-PuO2 is a porous medium for H2 migration. Besides, there have been considerably fewer studies on the hydrogen behaviors in the Pu-oxide matrix, and our current knowledge of the basic mechanisms therein is too limited to achieve an in-depth understanding of the Pu-hydriding induction period and establish a predictive model.

In this work, the first-principles calculations and ab initio atomistic thermodynamic method are performed to systematically study the hydrogen behaviors in the PuO2 matrix: (a) the stable existence states, (b) the detailed diffusion mechanism, and (c) the temperature- and pressure-driven thermodynamic dissolution mechanism of hydrogen in PuO2, aiming at clarifying the hydrogen resistance mechanism of PuO2.

2. COMPUTATIONAL METHODS

The first-principles calculations are performed using Vienna ab initio simulation package (VASP)20 with a Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation (GGA).21,22 Based on our previous work, the cutoff energy of the plane wave is set to 600 eV,23 and the 6s27s6p6d6f5d and 2s2p4 electrons of Pu and O are considered as the valence electrons, respectively.17,23–26 The ground state of PuO2 is calculated to be antiferromagnetic (AFM).27,28 Density functional theory (DFT)-D3 method is used to describe the van der Waals correlation and its validity has been approved.29–31 The Brillouin zone is sampled with a 6 × 6 × 6 Monkhorst–Pack k-point grid.32 The calculations will stop until the residual force on each atom is less than 0.01 eV/Å.

The strong onsite Coulomb repulsion among the Pu-5f electrons is described with the DFT + U scheme formulated by Dudarev et al.47 Within this scheme, the difference between the Coulomb energy U and the exchange energy J parameters, 

\[ U_{\text{eff}} = U - J \]

is significant for the total energy functional. The choice of reasonable U and J parameters are mainly based on an overall agreement between the experimental data and theoretical results of the basic properties of PuO2 and Pu2O3.

In 2008, we, among the first to perform the DFT + U study of Pu oxides, have carefully checked the (U, J) parameters and suggested the U_{\text{eff}} to be set at 4 eV with \( U = 4.75 \) eV and \( J = 0.75 \) eV.24 Since then, more and more properties of PuO2 and α-Pu2O3 were studied using bulk modulus, phonon spectra, optical property, thermal conductivity, point defect properties, and surface structural and thermodynamic properties, have been well described within the DFT + U framework by other theoretical researchers. Among these works, the reasonable U_{\text{eff}} value of 4 eV for PuO2 has been uniformly recognized and utilized, which is also utilized in this work (with \( U = 4.75 \) eV and \( J = 0.75 \) eV). However, the DFT + U studies of α-Pu2O3 have not provided a uniform understanding of the choice of U_{\text{eff}}.35,36,38,39 Zhang and coworkers presented the calculated results of the structural and optical properties of α-Pu2O3 with U_{\text{eff}} of 3 and 4 eV,36,38,39 Ao et al. used U_{\text{eff}} of 4 eV to calculate the energetics of Ga in Pu, PuO2, and Pu2O3.40 More recently, Ghosh et al. concluded that the experimental lattice parameters and electronic band gap of PuO2 and α-Pu2O3 can be predicted with U_{\text{eff}} of 4 eV.35 In view of this finding, we also calculate the incorporation energy (Ei) of H and H2 in α-Pu2O3 with U_{\text{eff}} of 3 eV, according to Figure 2 in ref 23. The calculations with U_{\text{eff}} of 3 and 4 eV reach the same conclusion that the hydrogen incorporation is endothermic and H2 incorporation is much more preferred in α-Pu2O3. From a quantitative point of view, for the most stable incorporation state of H, the difference of the calculated Ei with U_{\text{eff}} = 3 and 4 eV is only 0.03 eV, while for H2, there is no difference at all. Thus, the hydrogen behaviors in α-Pu2O3 can be reasonably described by U_{\text{eff}} either equaling 3 or 4 eV. Besides, to eliminate the metastable configurations of f electrons in DFT + U calculations, many theoretical methods have been proposed,33,46–49 among which the detailed analysis of the occupation matrices is the necessary step. In this work, we first estimate the total energy convergence according to the pre-existing calculated results and then carefully check the density of states and the electron occupation number in partial orbitals. The well-reproduced band gap and the relatively local occupation number of f electrons help to further affirm that the electronic metastable states can be avoided.

The calculated lattice constant of PuO2 is 5.42 Å with 0.02 Å deviation to experimental value (5.40 Å).25,50 As shown in Figure 1a, the Pu bond length (2.35 Å), Pu−O bond length (2.71 Å), and Pu−O−Pu angles (109.47°) are equal. According to the bonding properties, PuO2 crystal cell
be divided into eight small cages (pink cube in Figure 1a) and O anions in cages are marked with different colors. Each cage contains one tetrahedron structure (Figure 1b) of four Pu cations with O in the center, and the eight O anions form a hollow O-cube (purple cube in Figure 1a).

The hydrogen diffusion rate constant is calculated using harmonic transition state theory (hTST)

\[ k_{\text{hTST}} = \prod_{i=1}^{3N} \frac{\nu_i^\text{IS} \nu_i^\text{TS}}{\nu_i} e^{-\Delta \nu_i / k_B T} \]

Here, \( \nu_i^\text{IS} \) and \( \nu_i^\text{TS} \) are the mode vibrational frequencies of the initial state (IS) and the transition state (TS), respectively. \( \Delta \nu_i \) is the energy barrier between the initial state and final state, and the climbing image nudged elastic band method (CI-NEB) is used to calculate the energy barriers with three images between the initial and the final states. The overall rate constant is calculated by

\[ k = \sum_{i=1}^{3N} k_i \]

where \( k_i^{\text{Diff}} \) is the rate constant of the \( i \)th step.

The incorporation energy \( E_i \) of H in PuO₂ is calculated by

\[ E_i = E_{\text{PuO}_2+xH} - E_{\text{PuO}_2} - x/2E_{\text{H}_2} \] (1)

Here, \( E_{\text{PuO}_2+xH} \) and \( E_{\text{PuO}_2} \) are the total energy of bulk PuO₂ with \( x \)H, bulk PuO₂, and H₂, respectively.

The changes of Gibbs free energy (\( \Delta G \)) is calculated by "ab initio atomistic thermodynamic method"\(^{51,52} \), written as

\[ \Delta G(T, P) = (E_i - N \times \mu_{\text{H}_2}(T, P_{\text{H}_2}))/V \] (2)

\[ \mu_{\text{H}_2}(T, P_{\text{H}_2}) = \mu_{\text{H}_2}(T, P) + k_B T \ln(P_{\text{H}_2}/P_0) \] (3)

\[ \mu_{\text{H}_2}(T, P_0) = \Delta H_{\text{H}_2}(T, P_0) - T \Delta S_{\text{H}_2}(T, P_0) \] (4)

where \( \mu_{\text{H}_2}(T, P) \) is the chemical potential of H₂. As we mainly consider the dissolution heat of hydrogen in bulk PuO₂, in eq 2, \( V \) and \( N \) are the volume of bulk PuO₂ and the number of H₂ molecules in PuO₂, respectively. Under the approximation of ideal gas, the chemical potential of H₂ is shown as eq 4, with \( k_B \) and \( P_0 \) representing the Boltzmann constant and the partial pressure of H₂, respectively. Here, \( \Delta H_{\text{H}_2} \) and \( \Delta S_{\text{H}_2} \) are the changes of the enthalpy and the entropy of H₂ at standard state pressure \( P_0 \) with the temperature ranging from \( T \) to 0 K.

3. RESULTS AND DISCUSSION

3.1. Incorporation Properties of H and H₂ in PuO₂

All possible incorporation sites of H are considered and shown in Figure 2: (a) site in ABC (Figure 1b) area along the Pu\(^{4+}\)-O direction (sites in BCD, ACD, and ABD areas are the same as ABC); (b) site between two O anions; and (c) site in the center of O-cube. In this calculation, the vdW dispersion force upon H₂ is considered by the optPBE-vdW and DFT-D3 methods. As shown in Table 1, H incorporation in PuO₂ is endothermic and H prefers to be absorbed in the ABC area (Figure 2a) with or without vdW corrections. In Figure 2a, the corresponding incorporation energies are 0.97, 0.91, and 1.19 eV/H with DFT + U, DFT + U-D3, and DFT + U-optPBE methods, respectively. Here, DFT + U-D3 method gives the lowest incorporation energy, and its validity has been approved in previous work on Pu-oxide matrix and surface adsorption,\(^{31} \) thus it is employed in subsequent calculations. In Figure 2a, the H–O bond length is 0.99 Å and the incorporation causes the distortion of the tetrahedron structure with the Pu–O bond length changing about 0.13 Å. Actually, this hydrogen incorporation state is the same as that in ref 15. In the present work, we focus on distinguishing the adsorption states between atomic and molecular hydrogen; therefore, we further calculate the incorporation energies of two separated H atoms (2H) and one H₂ molecule in PuO₂.

Figure 3a–c depicts the 2H incorporation at preferred sites (shown in Figure 2a), binding to two O anions with the nearest-neighboring, next-neighboring, and third-neighboring distances, respectively. The relatively stable incorporation structure is 2H binding with O anions of nearest-neighboring distance (Figure 3b) and the corresponding incorporation energy is 0.82 eV/H, which is 0.09 eV lower than the single H incorporation (Figure 2a). The incorporation energy of H₂ is 1.12 eV/H₂, indicating that H₂ incorporation in PuO₂ is also endothermic as the incorporation of H and is slightly more favored than the latter.

Since H₂ needs to dissociate and then H probably penetrates into the close-grained PuO₂, we further discuss the formation probability of H₂ in PuO₂ by calculating the energy barrier of 2H recombination into H₂. As shown in Figure 4, the stable 2H incorporation structure (Figure 3b) is taken as the starting point and the calculated energy barrier is 1.15 eV, thus the difficulty of 2H recombination makes atomic H the preferred existence state in PuO₂.

The partial density of states (PDOSs) of the most stable incorporation states of H and H₂ are also calculated to investigate the interactions between H, H₂, and PuO₂. As
shown in Figure 5a, the PDOS reveals that the interaction between H and O anion is to some extent obvious around \(-8\) eV, and the band gap of PuO\(_2\) decreases by almost 50%. Whereas \(\text{H}_2\) incorporation only induces one single state (Figure 5b), indicating that \(\text{H}_2\) barely interacts with PuO\(_2\).

To compare the hydrogen incorporation properties with \(\alpha\)-Pu\(_2\)O\(_3\), we further investigated the incorporation energies of H, \(2\text{H}\), and \(\text{H}_2\) in the \(\alpha\)-Pu\(_2\)O\(_3\) crystal cell, and the calculated results are 1.53 eV/H, 1.58 eV/H, and 0.34 eV/H\(_2\), respectively.\(^{33}\) In \(\alpha\)-Pu\(_2\)O\(_3\), \(^{33}\) a cell of dimension \(\sim11\) Å was used, while a cell of dimension \(\sim5.4\) Å is used in this work, which is small. Because of the periodic boundary condition applied in routine DFT calculations of defect behavior, there are cross-boundary effects and defect–defect interactions.

Thus, we further calculate the incorporation energies of H, \(2\text{H}\), and \(\text{H}_2\) in the \(2 \times 2 \times 2\) supercell of PuO\(_2\), which is comparable in dimension to the \(\alpha\)-Pu\(_2\)O\(_3\) crystal cell, and the corresponding results are 0.48 eV/H, 0.64 eV/H, and 0.90 eV/H\(_2\), respectively. These results clarify the different incorporation behaviors of hydrogen in \(\alpha\)-Pu\(_2\)O\(_3\): (i) H incorporation is much more endothermic than H\(_2\) incorporation in \(\alpha\)-Pu\(_2\)O\(_3\) and (ii) H recombines into H\(_2\) spontaneously and H\(_2\) is the preferred existence state in \(\alpha\)-Pu\(_2\)O\(_3\). Due to the significant differences in the lattice structure and oxidation state, namely, PuO\(_2\) is airtight and reducible but \(\alpha\)-Pu\(_2\)O\(_3\) is porous and irreducible for hydrogen, the subsequent hydrogen diffusion and dissolution behaviors in PuO\(_2\) are expected to be quite
different from those in $\alpha$-Pu$_2$O$_3$, which may contribute to the hydrogen resistance mechanism of PuO$_2$.

3.2. Diffusion Behaviors of H in PuO$_2$. As discussed above, H is the preferred existence state in PuO$_2$ and the reformation of H$_2$ is difficult; hence, we mainly focus on the diffusion behavior of H in PuO$_2$. As shown in Figure 6, H diffusion along O atoms in the PuO$_2$ matrix and the complete diffusion path includes two steps: (I) taking the stable incorporation site depicted by Figure 2a as the initial state (IS$_1$), H first migrates along the magenta O in up-cage to the first final state (FS$_1$), with H binding to the green O in down-cage and pointing to the inside of cube (and (II) then starting from FS$_1$ (IS$_2$), H rotates through one quadrilateral (consisting of green, cyan O anions, and two Pu cations), and finally points to the neighboring O-cube (FS$_2$).

As shown in Figure 6, the main diffusion barrier of H (at TS$_1$) is calculated to be merely 0.13 eV, which is much lower than the endothermic incorporation energies of hydrogen in PuO$_2$ (in Table 1). Our recent work revealed that both H and H$_2$ diffusions in $\alpha$-Pu$_2$O$_3$ are feasible and the energy barriers are 0.67 and 0.66/0.53 eV, respectively. Since it is hard for hydrogen to recombine to H$_2$ (Figure 4), we can see that the hydrogen diffusion in PuO$_2$ has no alternative but as H, however, it is certainly easier than H or H$_2$ diffusion in $\alpha$-Pu$_2$O$_3$. At this point, the hydrogen diffusion mechanism in PuO$_2$ is to some extent an interesting exception, which is mainly due to the fact that the highly endothermic incorporation of H in PuO$_2$ can keep the incorporation system at the high potential and unstable levels, as shown in Figure 7.

![Figure 7](https://example.com/figure7.png)

Figure 7. Sketch of hydrogen behavior in the induction period of Pu hydriding in intact PuO$_2$ and $\alpha$-Pu$_2$O$_3$. The solid and dot lines in steps (i) and (ii) represent the data in refs 17 and 18, respectively.

The diffusion rate constant and coefficient of H at 300 K are calculated and shown in Table 2. The diffusion rate constants of diffusion path (I) and (II) have the same magnitude, the diffusion coefficients are also comparable. The overall rate constant $k_{\text{overall}}$ of H in PuO$_2$ is about eight orders of magnitude larger than that of H$_2$ diffusion in $\alpha$-Pu$_2$O$_3$, which further confirms that H diffusion in PuO$_2$ is much easier than H$_2$ in $\alpha$-Pu$_2$O$_3$. Based on the current theoretical results, we conclude that once squashing in PuO$_2$, the H diffusion on a high-potential-energy surface is not difficult, so that the hydrogen resistance mechanism of PuO$_2$ is not the bulk-diffusion-limited type.

3.3. Dissolution Properties of H in PuO$_2$. In this subsection, we mainly discuss the thermodynamic dissolution mechanism of H atoms in PuO$_2$. According to Section 3.1, each O at the center of Pu-tetrahedron provides four equivalent incorporation sites for H. As shown in Figure 8, we consider the uniform dissolution of H atoms in eight small cages with the O/H ratio of 1:1 (a), 1:2 (b), 1:3 (c), and 1:4 (d). The corresponding H incorporation energies are 0.63, 0.97, 1.28, and 1.55 eV/H, respectively (Table 3). After relaxation, the bulk structures are slightly distorted with the increasing H atoms, and the dissolved hydrogen species are in three states: H$_2$ (orange ball), H bonding with O anions (pink ball), and H in O-cube (purple ball). Meanwhile, it is obvious that the dissolved hydrogen (H$_2$ and H) will prefer to distribute within the interlayers of the O–Pu–O films alone (111) direction (in Figure 8), which also can be found in the layered $\alpha$-Pu$_2$O$_3$. Besides, in Table 3, $N_{\text{H}}$ increases with the increasing H, while $N_{\text{O-H}}$ and $N_{\text{Pu-H}}$ remain almost unchanged, indicating that the final dissolution state of hydrogen is probably a mixture of H and H$_2$.

Due to the endothermic dissolution of H in PuO$_2$, the “ab initio thermodynamic method” is performed to discuss the influence of external hydrogen pressure ($P_{\text{H}}$) and temperature on the dissolution mechanism. The changes of Gibbs free energy ($\Delta G$) are calculated by eq 2, and the entropy and enthalpy of the H$_2$ molecule are searched in thermochemical tables. At $P_0 = 1$ bar, $\mu_{H_2}(T,P_0)$ equals to $-0.32$ eV (300 K) and $-0.46$ eV (400 K), respectively.

As shown in Figure 9, (i) when $P_{\text{H}} < 3.31 \times 10^{26}$ Pa, dissolution of H in PuO$_2$ is unfeasible, and (ii) for $P_{\text{H}} > 3.31 \times 10^{26}$ Pa, H dissolution is feasible, and the solubility increases to 16H as $P_{\text{H}}$ becomes larger than 3.26 $\times 10^{29}$ Pa. We further investigate the influence of temperature, supposing that the structure and solubility of dissolved hydrogen will not change distinctly within 400 K. At 400 K, the thermodynamic dissolution mechanism does not change, while $P_{\text{H}}$ reduces about three to five orders of magnitude. Thus, both $P_{\text{H}}$ and temperature can promote the H dissolution in PuO$_2$.

Our recent work revealed that at 300 K, the H$_2$ dissolution in $\alpha$-Pu$_2$O$_3$ is more feasible with the lowest equilibrium $P_{\text{H}}$ of $1.20 \times 10^{14}$ Pa, which is about ten orders of magnitude smaller than H in $2 \times 2 \times 2$ PuO$_2$ supercell of $3.05 \times 10^{21}$ Pa. When compared with the uniform dissolution of H atoms with the O/H ratio of 1:1, the dissolution of low-concentration H with the O:H ratio of 64:1 is easier to achieve. These results further reveal that the intact PuO$_2$ layer works as a protective screen against Pu hydriding, mainly because it can suppress the H$_2$ dissociation on the surface, H-penetration into the subsurface, and the subsequent H-dissolution in the bulk PuO$_2$.

4. CONCLUSIONS

The micromechanisms of the hydrogen behaviors in the PuO$_2$ matrix are systematically investigated using the first-principles calculations and ab initio thermodynamic method within DFT $+ \ U$ and DFT-D3 schemes. We find that the incorporation, diffusion, and dissolution behaviors of H and H$_2$ in PuO$_2$ are
all endothermic. Also, the recombination barrier of H\textsubscript{2} is 1.15 eV, which is opposite to the spontaneous formation of H\textsubscript{2} in α-Pu\textsubscript{2}O\textsubscript{3}; thus, H is the preferred existence state in PuO\textsubscript{2}. The diffusion barrier of H in PuO\textsubscript{2} is 0.13 eV, which is smaller than that of H\textsubscript{2} in α-Pu\textsubscript{2}O\textsubscript{3}. Based on a series of theoretical studies, we conclude that the main hydrogen behaviors in PuO\textsubscript{2} and α-Pu\textsubscript{2}O\textsubscript{3} are quite different, but not involved with chemical reactions. Also, the primary hydrogen resistance mechanism of PuO\textsubscript{2} can be attributed to the combination of surface-reaction-limited and the bulk-solubility-limited effects. These conclusions are very important for modeling the complex induction period of Pu hydriding.

Table 3. Calculated Incorporation Energy ($E_i$) and Number of H\textsubscript{2} ($N_{H_2}$), H Bond with O Anions ($N_{O-H}$), and H in O-cube ($N_{H\text{hole}}$) of Figure 8

| O/H | 1:1 | 1:2 | 1:3 | 1:4 |
|-----|-----|-----|-----|-----|
| $E_i$ (eV) | 5.04 | 15.52 | 30.72 | 49.60 |
| $E_i/H$ (eV/H) | 0.63 | 0.97 | 1.28 | 1.55 |
| $N_{H_2}$ | 2 | 5 | 9 | 13 |
| $N_{O-H}$ | 4 | 5 | 5 | 5 |
| $N_{H\text{hole}}$ | 0 | 1 | 1 | 1 |

Figure 9. Generic free energy plot for H dissolution mechanisms in equilibrium with $P_{H_2}$, $P_{H_2}$ at a critical point of $\Delta G < 0$, and dissolution mechanism changes are labeled at 300 K (in black) and 400 K (in brown).

Notes
The authors declare no competing financial interest.

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