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Co-adsorption of O_2 and H_2O on α-uranium (110) surface: A density functional theory study*

Xin Qu(瞿鑫), Ru-Song Li(李如松)†, Bin He(何彬), Fei Wang(王飞), and Kai-Long Yuan(袁凯龙)

Xi'an High Technology Institute, Xi'an 710025, *China*

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First-principles calculations based on density functional theory corrected by Hubbard parameter U (DFT+U) are applied to the study on the co-adsorption of O_2 and H_2O molecules to α-U(110) surface. The calculation results show that DFT+U method with $U_{\text{eff}} = 1.5$ eV can yield the experimental results of lattice constant and elastic modulus of α-uranium bulk well. Of all 7 low index surfaces of α-uranium, the (001) surface is the most stable with lowest surface energy while the (110) surface possesses the strongest activity with the highest surface energy. The adsorptions of O_2 and H_2O molecules are investigated separated. The O_2 dissociates spontaneously in all initial configurations. For the adsorption of H_2O molecule, both molecular and dissociative adsorptionsoccur. Through calculations of co-adsorption, it can be confirmed that the inhibition effect of O_2 on the corrosion of uranium by water vapor originates from the preferential adsorption mechanism, while the consumption of H atoms by O atoms exerted little influence on the corrosion of uranium.

Keywords: co-adsorption, α-U(110) surface, DFT+U, inhibition mechanism

PACS: 65.40.gp, 68.35.–p, 71.15.Mb **DOI:** 10.1088/1674-1056/27/7/076501

1. Introduction

Uranium is an important and irreplaceable material in the field of nuclear industry for its excellent properties. However, due to the small energy gap between the 5f and 6d orbit as their levels are of the same order of magnitude (∼6 eV), the 5f and 6d orbit are easily hybridized, leading to a wide range of oxidation states of uranium varying from +2 to +6 oxidation states,[1] which indicates active chemical properties of uranium. Thus, uranium is easily corroded, which causes many problems in the application and storage of uranium. Therefore, uranium corrosion is an issue of great significance and many investigations have been done.[2–8] Meanwhile, in past decades, a great deal of effort has been devoted to the anti-corrosion studies of uranium.[9–14]

As is well known, O_2 and H_2O are two common oxidants in atmosphere, so their interactions with uranium have received lots of attention. In recent years, many experimental studies have been carried out on oxidation of uranium by O_2 and H_2O. Among these studies, many efforts have been devoted to the kinetics of reaction with H_2O and O_2[15–21] in different temperature ranges. On the basis of these studies, Haschke[22] made a detailed review and argued that the moisture could enhance the corrosion rate due to the fact that a water-catalyzed cycle was formed in the environment with air and water vapor coexisted, but the oxygen dissolved in water would suppress the corrosion rate of uranium. The surface science investigation is an important subject in material science and so is the study on uranium. The reaction of hydrogen and steam with uranium surface at room temperature was studied by combining modulated molecular beam scattering, temperature programmed desorption, and atomic force microscopy experiments.[23] To reveal the fundamental mechanism of interaction of water with uranium, Manner *et al.*[24] investigated the interactions of D_2O with uranium at 85 K and 300 K. They observed that D_2O dissociated into OD groups, O atoms and D atoms at 85 K with low exposures ($\leq$ 0.5 L). At high exposures, both dissociative and molecular adsorption would happen. D atom desorption in the form of hydrogen as temperature increases was also observed.

The radiation and chemical toxicity of uranium presents a challenge to experimental study. Fortunately, with the development of density functional theory (DFT) and large-scale parallel computer, modeling and simulation on computer has gradually become an important method besides experiments. The DFT is a theory within quantum mechanism, its calculated results conform well to experimental results in most systems, so it has been widely applied to the studies on materials science.[25–30] The strongly correlated 5f electrons of uranium cause abnormal properties, DFT+U method can improve accuracy in treating 5f electrons. Beridze *et al.*[31] performed DFT+U calculations of uranium and uranium compounds, and the results demonstrated that the Hubburd parameter U could be estimated by thermochemistry data. The interaction between uranium atom and H_2O molecule is a fundamental mechanism of the reaction of uranium with water, and the mechanism was investigated by DFT calculations or combining experiments.[32,33] When it comes to the surface science research on the uranium surface, the adsorption of H_2O,

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†Corresponding author. E-mail: rusong231@126.com

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O_2, and O atom to uranium surface was studied based on DFT method.[34,35]

To the best of our knowledge, although there were very few studies on the co-adsorption,[36] no researches on the co-adsorption of H_2O and O_2 molecules to the uranium surface were reported. All reported DFT studies on the corrosion of uranium concentrated on either H_2O or O_2 adsorption to uranium surface. In this work, we carry out the first-principles calculations on the co-adsorption of H_2O and O_2 molecules to uranium surface based on DFT+U method with the hope of explaining the experimental results of uranium corrosion in moist air.

2. Method

All calculations in the present paper are performed using Vienna *ab-initio* simulation package (VASP) code with projector augmented wave (PAW) together with ultra-soft pseudopotentials method. We perform a convergence test on the cutoff energy for plane-wave basis in a range from 400 to 600 eV in the steps of 50 eV. The calculated results suggest that 500 eV is a reasonable value. The treatment of exchange–correlation functional is a critical factor for DFT calculations, and we use the revised Perdew–Burke–Ernzerhof functional within generalized gradient approximation (GGA) scheme.[37–40] Within pseudopotential formalism, the nucleus and core electrons are treated as being screened and only the valence electrons are treated explicitly. For U, O, and H atoms, the $6s^2 6p^6 7s^2 5f^3 6d^1$, $2s^2 2p^4$, and $1s^1$ electrons were treated as valence electrons. The k-point mesh for integration over Brillouin zone is generated by Monkhorst–Pack method.[41] A $7\times7\times7$ k-point mesh is used for optimizing α-uranium conventional cell, as well as O_2 and H_2O molecular, while $3\times5\times1$ k-point grid for α-uranium surface and the adsorption system. Considering the induced dipole moment form one-sided adsorption model, dipole correction is introduced into the adsorption system. Conjugated gradient algorithm for the ionic relaxation in VASP code was implemented by Brent's numerical algorithm, and the error would occur when the system was already highly converged. Because it could not interpolate the corrections of the next atomic position within the numerical accuracy since it simply would be so small. Thus, quasi-Newton algorithm is used to obtain the ground state of the conventional cell of α-uranium for its much higher efficiency than conjugated gradient algorithm as the system has almost reached equilibrium. However, the quasi-Newton algorithm converges slowly to an equilibrium position when the initial states were far from equilibrium, so conjugated gradient algorithm is used for the adsorption system considering that it could find the ground state in a wide spatial range.

Uranium is an actinium element characterized by partially filled 5f electrons. Due to the strongly correlated interaction among 5f electrons, standard DFT cannot capture the proper physics of the 5f electrons as it underestimates the on-site Coulomb repulsion interaction among localized 5f electrons, leading to deviation of the calculated results from experimental results. The DFT+U method is proposed to improve the description of the behavior of strongly correlated electrons.[26,29] This method could yield a reasonable result with an adjustable Hubbard parameter U deduced from constrained local density functional or random phase approximation. In this paper, we adopt the simplified approach proposed by Dudarev *et al.*[42] In this approach, the Hamiltonian of 5f electrons can be given by

$$E_{\mathrm{LSDA}+U} = E_{\mathrm{LSDA}} + \frac{(U-J)}{2}\sum_{\sigma}[\mathrm{Tr}\rho^{\sigma} - \mathrm{Tr}(\rho^{\sigma}\rho^{\sigma})], \quad (1)$$

where E_{LSDA} is the energy within standard DFT scheme; parameter U represents the on-site Coulomb repulsion among 5f electrons, and J is the exchange parameter; σ is the given projection of spin. As shown in Eq. (1), we can obtain that what takes effect finally is U_{eff} (U–J). In the determination of suitable U_{eff} value for the α-uranium system, we only changed the value of U while J was fixed to 0 eV.

The α-uranium surface energy and the adsorption systems were studied by using $p(2\times1)$ surface slab cell with 6 atomic layers. To eliminate the self-interaction of surface atoms actually at the same position, resulting from the periodic reduplicative slab cell along the z direction, the vacuum thickness is set to be big enough as 15 Å to obtain a reliable simulation of the real surface. When carrying out ionic relaxation, the atoms in the top two layers of α-uranium and the adsorbate atoms are set to be free in all three degrees of freedom while others in the bottom four layers were fixed.

In the solid physics, surfaces must be intrinsically less energetically favorable than the bulk of a material, otherwise, there would be a driving force for surfaces to be broken. The surface energy may, therefore, be defined as the excess energy at the surface of a material compared with that in the bulk. In the first-principles, the surface energy E_{sur} could be calculated by subtracting the energy of an equivalent number of bulk atoms in equilibrium states from the energy of the surface atoms obtained from slab model and dividing this number by twice the surface area $2A$, i.e.,

$$E_{\mathrm{sur}} = (E_{\mathrm{slab}} - NE_{\mathrm{bulk}})/2A, \quad (2)$$

where E_{slab} is the energy of atoms in the slab model, N is the number of atoms in slab cell, and E_{bulk} is the energy of atoms in equilibrium α-uranium.

3. Results and discussion

3.1. Parameter U_{eff} and surface energy

It should be cautious to determine the value of U_{eff} as it is of crucial importance for DFT+U calculations in Dudarev's

approach. That is because a reasonable description of the system depends on an appropriate U_{eff}, an inappropriate U_{eff} may yield unreasonable results, so the determination of U_{eff} is an important part of our study. The Hubbard parameter U represents the average strength of on-site Coulomb repulsion interaction among 5f electrons, which will change in different chemical environments. In theory, different chemical environments represent different electronic structures and populations, thus different values of U. It could be demonstrated by Refs. [24], [40], and [41], as these studies suggest that for different uranium compounds, the values of parameter U are different.

Considering that elastic modulus is sensitive to the bonding interaction between atoms, therefore it could be selected as a criterion to judge whether the calculation result is reasonable and accurate. In the present paper, we use the lattice constants and elastic modulus to determine the value of U_{eff} of α-uranium. Firstly, standard DFT calculations are performed ($U = 0$ eV), then we carry out DFT+U calculations with U_{eff} varying in a range from 1.2 eV to 1.8 eV, and the results are listed in Table 1.

The experimental data listed in Table 1 are obtained from the experiments carried out in the 1950s and 1960s, and there are no newer data. In addition, we should notice that the results obtained from experiments carried out by different methods are different, so we do not view these experiment data as an absolute criterion but as a reference interval to determine the appropriate U_{eff} value. By comparing with the experimental results, we can find that the calculated results of lattice constants and elastic moduli are in a relatively reasonable interval given by experiments if U_{eff} equals 1.5 eV. Therefore, U_{eff} is set to be 1.5 eV in the following calculations.

Table 1. Lattice constants and elastic moduli with different U_{eff} values. Units of lattice constant and elastic moduli are Å and Mbar respectively. Experimental lattice constants of α-uranium are cited from Ref. [43]; Experiment[b] is carried out at room temperature(25 °C) and data of experiment[c] are obtained from linear extrapolation to 0 K.

U_{eff}	a	b	c	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
	2.807	5.898	4.922	3.01	2.25	3.59	1.53	1.27	1.04	0.45	0.25	1.30
1.2	2.894	5.889	5.014	2.27	2.04	3.17	1.33	0.93	0.82	0.63	0.22	1.25
1.3	2.897	5.889	5.019	2.22	2.00	3.08	1.31	0.91	0.82	0.64	0.23	1.24
1.4	2.902	5.890	5.026	2.19	1.97	3.02	1.27	0.90	0.79	0.61	0.20	1.22
1.5	2.909	5.892	5.032	2.20	1.96	2.99	1.24	0.88	0.78	0.60	0.19	1.21
1.6	2.914	5.894	5.039	2.22	1.95	2.94	1.21	0.87	0.77	0.60	0.17	1.20
1.7	2.919	5.897	5.045	2.24	1.93	2.89	1.17	0.85	0.75	0.60	0.19	1.19
1.8	2.924	5.899	5.052	2.26	1.90	2.84	1.14	0.82	0.74	0.60	0.16	1.18
Expt[a]	2.836	5.866	4.936									
Expt[b]				2.15	1.99	2.67	1.24	0.73	0.74	0.47	0.21	1.08
Expt[c]				2.10	2.15	2.97	1.45	0.94	0.87			

[a]Ref. [43]. [b]Ref. [44]. [c]Ref. [45].

Energetically, the lower the energy, the more stable the system will be. To the best of our knowledge, the (001) surface of α-uranium has been investigated extensively.[39,46–48] However, there are no systematical investigations on all seven low index surfaces, we perform calculations on the surface energies of the seven low index surfaces to obtain comprehensive knowledge about the surface energy of α-uranium low index surface. The atoms in crystal surface are located in a non-equilibrium force field, and they are different from the atoms in bulk which are located in an equilibrium or a meta-equilibrium crystal field, and the surface atoms will relax to equilibrium positions in the direction toward the minimum energy. Therefore, to obtain the surface energy of α-uranium, we relax the α-uranium surfaces to the lowest energy states at first. After the surface cells with 6 atomic layers reach the ground states, we calculate the surface energies of the seven low index surfaces according to Eq. (2), and the results are presented in Table 2.

As shown in Table 2, the (001) surface is the most stable surface with the lowest surface energy, while the (110) surface is the most unstable surface in all seven low index surfaces, so the (110) surface will be more active than the other six low index surfaces in general. Due to the strongest chemical activity, the (110) surface of α-uranium is most likely to be oxidized. Hence, the study on the corrosion of (110) surface can perform the most rigorous evaluationofthe corrosion resistance of α-uranium surface.

Table 2. Surface energiesof seven low index surface of α-uranium

Surfaces	001	010	011	100	101	110	111
E_{sur}/J·m^{-2}	1.72	2.03	1.87	1.84	1.79	2.26	1.75

3.2. Adsorption of O_2 and H_2O to α-U(110) surface

As discussed in the former section, there have been few types of research on the adsorption of O_2 and H_2O molecules to the α-U(110) surface to date. In this paper, we calculate the adsorption behavior of O_2 and H_2O molecules on α-U(110) surface. On the one hand, the research could act as a supplement to extend the studies of surface corrosion of α-uranium

surface. It is more important, on the other hand, that it laid a foundation for the following studies on the co-adsorption of O_2 and H_2O molecules to α-U(110) surface.

To study the adsorption behavior of O_2 and H_2O molecules to α-U(110) surface, we use 2×1 extended surface slab cell with 24 uranium atoms aggregating. In general, according to the minimum energy principle, the surface adsorption of molecules and atoms are more likely to occur at high symmetric sites. As illustrated in Fig. 1, four high symmetric sites were taken into account, i.e., the top site, hollow site, short-bridge site, and long-bridge site, and were denoted as T, H, SB, and LB, respectively. We carry out the calculations on the adsorption of O_2 molecules at first. Three different orientations of O_2 molecules are taken into consideration at each of four high symmetry adsorption sites, and 12 initial adsorption configurations are constructed.

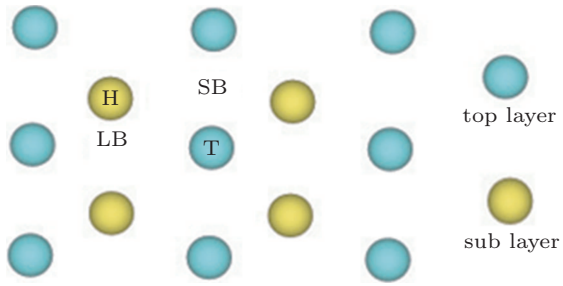


Fig. 1. Top view of adsorption sites on α-U(110) surface.

After optimization, we find that O_2 molecules dissociate spontaneously into two O atoms in all 12 initial adsorption configurations with the adsorption energy (subtracting the total energy of relaxed adsorption system from the sum of total energy of optimizing O_2 molecule and α-U(110) surface) varying from 10.88 eV to 12.60 eV. The adsorption energy obtained in the present paper is bigger than the result of Huang *et al.*[48] It could be accounted for the fact that the (110) surface is more active than the (001) surface. The surface that Huang *et al.* studied is the lowest energy surface, while the highest energy surface is investigated in our work. This phenomenon also demonstrates that the (110) surface is more easily corroded than (001) surface. In the most stable adsorption configuration of O_2, two O atoms dissociating from the O_2 molecule are located at two adjacent short bridge sites as depicted in Fig. 2. The dissociated O atoms have a strong bonding interaction with the two nearest uranium atoms by forming U–O–U bond. Due to the strong bonding interaction of O atoms with U atoms, the U atoms adjacent to the O atoms move outwardly at most 0.09 Å relative to the previous equilibrium position.

Taking into account the more complex structure of H_2O molecule than O_2 molecule, we consider four different orientations of H_2O molecules at each adsorption site. The chemical activity of H_2O molecule is not so strong as O_2 molecule, and the interaction of H_2O molecule with U atoms is weaker than that with O_2 molecule. Therefore, among 16 initial adsorptions, only 3 initial configurations undergo the dissociation adsorption while others adsorbed to α-U(110) surface molecularly. For molecular adsorption, the adsorption energy is in a range from 0.53 eV to 0.68 eV, indicating that the molecular adsorption of H_2O molecule to α-U(110) surface is physical adsorption rather than chemical adsorption. Here we discuss and analyze the dissociation adsorption of H_2O molecule. We find that H_2O molecule completely dissociates into one O atom and two H atoms if the two H atoms in H_2O molecule both direct to the [010] direction when adsorbed to the short-bridge site horizontally, and 4.22 eV adsorption energy is released. As shown in Fig. 3(a), the dissociated O atom is adsorbed to the short bridge site stably, while the other two H atoms are adsorbed to the adjacent short-bridge and long-bridge site. However, partial dissociation happens when two H atoms of H_2O molecule direct to the [100] direction while H_2O molecule is horizontally adsorbed to the short-bridge site. As shown in Fig. 3(b), one H atom and OH group are formed with an adsorption energy of 2.42 eV. Figure 3(c) shows another stable partial dissociation system of H_2O molecule. This partial dissociation takes place when H_2O molecule is initially adsorbed vertically to the short-bridge site with its two H atoms pointed to [010] direction, the adsorption energy is 2.57 eV and it is of the same order of magnitude as the former partial dissociation one. As illustrated in Fig. 3(c), OH group is adsorbed vertically to the short-bridge site and H atom is located at the short-bridge site nearest to the OH group.

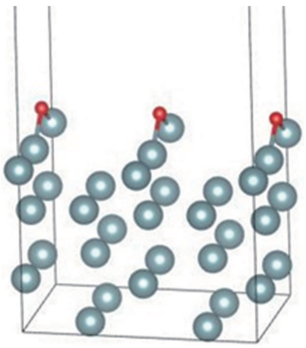


Fig. 2. The most stable adsorption configuration of O_2.

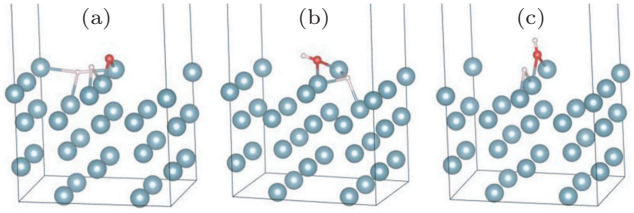


Fig. 3. Stable dissociation adsorption of H_2O.

3.3. Co-adsorption of O_2 and H_2O molecule to α-U(110) surface

Experimental research performed by Haschke *et al.*[16] proved that the O_2 dissolved in vapor can suppress the rate of uranium corrosion in most air and water vapor. To account for this phenomenon on an atomic scale, we study the co-adsorption of O_2 and H_2O molecules to the α-U(110) surface, and then make preliminary discussion on the inhibition mechanism by O_2 molecule. At the initial stage of uranium corrosion in oxygen and water vapor, there are two possible mechanisms of inhibition effect from O_2 molecule. One possibility is that O_2 molecule is adsorbed preferentially to the α-U(110) surface due to its much stronger chemical activity than H_2O molecule, which poses an inhibition effect on the subsequent adsorption of H_2O molecules. Another possibility is that the dissociated O atoms consume the dissociated H atoms by bonding into OH group. The uranium hydride, which could react with H_2O at an extreme speed, can be formed in the reaction of dissociated H atoms with uranium. The consumption of H atoms can suppress the formation of uranium hydride, and therefore suppressing the corrosion of uranium by water vapor.

3.3.1. Preferential adsorption of O_2 molecule

Firstly, we carry out the calculation of the preferential adsorption of O_2 molecule. A system always relaxes spontaneously toward minimum energy state, so we use the most stable relaxed adsorption system of O_2 molecule as an adsorption substrate of the subsequent H_2O molecule. Taking into consideration the fact that only three initial configurations, where H_2O molecules located at short-bridge site, undergo dissociation, we construct three initial co-adsorption configurations with H_2O located at the same position as these three configurations.

After ionic relaxation, H_2O molecule partially dissociates into one H atom and OH group in the initial configuration where H_2O molecule is adsorbed horizontally with the two H atoms directing to the [010] direction. In the dissociation process, 2.50 eV adsorption energy is released. By comparison, for the same adsorption configuration of H_2O molecule alone, H_2O molecule completely dissociates into one O atom and two H atoms with the adsorption energy up to 4.22 eV. Apparently, the preferentially adsorbed O_2 molecule weakens the interaction strength between H_2O molecule and uranium atoms and thus hindering the subsequent adsorption of H_2O molecule. We also observe obvious inhibition effect by the preferentially adsorbed O atoms in the initial configuration where H_2O molecule adsorbs horizontally to the short-bridge site while the two H atoms direct to [100] direction. In the same initial configuration of H_2O molecule adsorption alone, H_2O molecule partially dissociates into one H atom and OH group with 2.42 eV adsorption energy released. However, due to the preferential adsorption of O_2 molecule, H_2O molecule does not undergo dissociation but is adsorbed to α-U(110) surface molecularly instead. The adsorption energy is 0.51 eV that is much smaller than that of dissociation adsorption.

The inhibition mechanism of the preferential adsorption of O_2 molecules can be understood from different aspects. As discussed in Subsection 3.2, not only the dissociated atoms of O_2 molecule, but also the dissociated atoms of H_2O molecule tend to be adsorbed to the short-bridge site. However, the dissociated O atoms of preferentially adsorbed O_2 molecule occupy the most favorable adsorption site, thus the preferential adsorption of O_2 molecule inhibits the subsequent adsorption of H_2O molecule.

To explain the inhibition mechanism by the preferential adsorption of O_2 on an electronic scale, we calculate the projected density of state (PDOS) of clean α-U(110) surface, the most stable adsorption configuration of O_2 molecule alone, the adsorption of H_2O alone, and the co-adsorption of O_2 and H_2O molecules. The results are presented in Fig. 4. Comparing Fig. 4(a) with Fig. 4(b), one can find that the PDOS of 5f and 6d orbit of the uranium atoms around the Fermi level decrease after the adsorption of O_2 molecule. At the same time, two new peaks of 5f and 6d orbits form around -5 eV energy level, which overlaps with those of 2p orbit of O atoms. Taking into account the fact that the distance between O atom and its nearest uranium is smaller than U–O bond of UO_2, it can be confirmed that some of 5f and 6d electrons of uranium atoms hybridize with O 2p orbitals, resulting in the formation of strong chemical bonds. Due to the bonding interaction with O 2p orbitals, bonding energy is released. Therefore, the 5f and 6d electrons hybridized with O atoms move to a much lower energy level, leading to the formation of two new peaks of 5f and 6d orbitals around -5 eV. From Fig. 4(b) one can see that the 6d orbit peak around -5 eV is nearly double that of 5f orbit, indicating that although 5f electrons exhibit chemical activity in the reaction with O_2 molecule, the chemical activity of 6d electrons plays a dominant role. Figure 4(c) shows the PDOSs of the adsorption of H_2O alone, it can be seen that bonding interactions of 6d electrons with OH group and O atoms exist, while the 5f electrons are inert. The conclusion is the same as that from the work of Li *et al.*[49] As shown in Figs. 4(b) and 4(c), the adsorption of H_2O molecule does not exert influence on the bonding interacting between O atoms and uranium atoms, because the interaction peak of O atoms and uranium atoms does not change after the adsorption of H_2O molecule. This phenomenon demonstrates that the chemical activity of O atoms is much stronger than that of H_2O molecule in the reaction with uranium. In summary, 5f and 6d electrons each play a dominant role in the reactions of uranium with O_2 molecule and also with H_2O molecule, hence, there is a competition be-

tween O_2 and H_2O molecules when co-adsorbed to uranium surface. Due to the much stronger chemical activity, O_2 dominates the competition, and inhibits the subsequent adsorption of H_2O molecule.

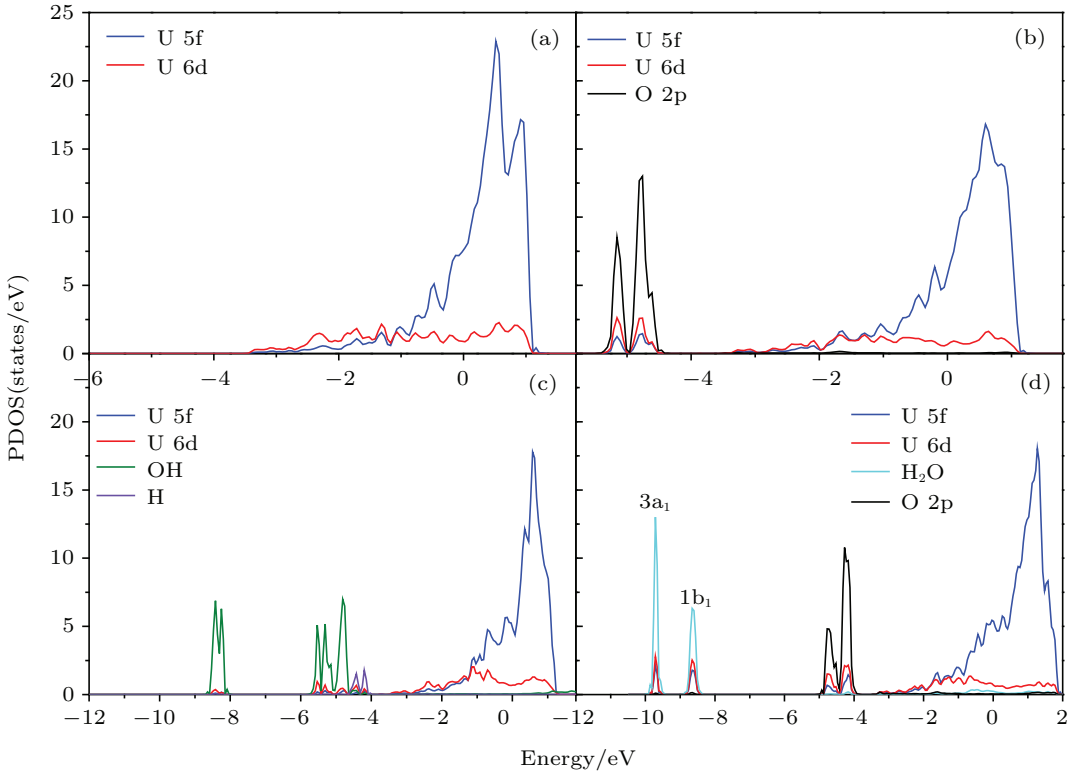


Fig. 4. Plots of PDOS versus energy for (a) clean α-U(110) surface, (b) the most stable adsorption configuration of O_2 after optimization, (c) adsorption of H_2O molecule alone, (d) co-adsorption of H_2O and O_2 molecules in the pattern of preferential adsorption of O_2 molecule.

3.3.2. Consumption of dissociated H atoms

Another possible inhibition mechanism is the consumption of the dissociated H atoms. The dissociated O atoms of O_2 molecules react with the dissociated H atoms of H_2O molecules, thus reducing the formation of uranium hydride. It can also be viewed as the inverse process of the dissociation of H_2O molecule. Hence, the reaction rate is slowed down. We use the most stable adsorption configuration of H_2O molecule as the co-adsorption substrate, and O atoms are placed near the H atoms in the initial configuration.

The computational results suggest that OH group forms in only one initial configuration in all the six initial configurations. This could be explained by the fact that the bonding of O atoms with uranium atoms is more energetically favorable than with H atoms. That is because the interaction between uranium atoms and O atoms is much stronger than that between uranium atoms and H atoms. Therefore, we may draw the conclusion that this inhibition mechanism is not the main cause of the suppression of corrosion of uranium, and the preferential adsorption of O_2 molecule is the dominant inhibition mechanism.

4. Conclusions

In this paper, DFT+U method is applied to the investigation on the co-adsorption of O_2 and H_2O molecules to α-U(110) surface. At first, we study the lattice constants and elastic moduli as a function of U_{eff}. Results suggest that the DFT+U method cannot completely yield all the experiment data, though it can significantly improve the accuracy of the calculations. The calculated results indicate that 1.5 eV is a suitable value of U_{eff}. On this basis, we systematically investigate the surface energies of the 7 low-index surfaces of α-uranium. The lowest energy surface of α-uranium is the (001) surface and the highest one is the (110) surface. The surface energies of the two surfaces are 1.72 J·m^{-2} and 2.26 J·m^{-2}, respectively.

In order to extend the surface study on α-uranium and lay the foundation for the study on co-adsorption of O_2 and H_2O molecules, the adsorption of O_2 and H_2O molecules to α-U(110) surface alone are investigated. After ionic relaxation, all initial adsorption configurations of O_2 molecules undergo the dissociation with the adsorption energy varying from 10.88 eV to 12.60 eV. When the adsorption of H_2O molecule happens, H_2O molecules dissociate while being adsorbed to the short-bridge site initially; for other initial adsorption con-

figurations, molecular adsorption occurs.

In this work, the inhibition mechanism of O_2 molecule in the corrosion of uranium by water vapor is studied. Although the dissociated O atoms are likely to bond with dissociated H atoms into OH group, the possibility is relatively small and it is not the main cause of the inhibition effect. The main inhibition effect comes from the preferential adsorption of O_2 molecule. The O_2 molecule preferentially occupies the most favorable adsorption site, and inhibits the adsorption of subsequent H_2O molecules through its strong bonding interaction with uranium atoms.

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