



Chemisorption of a hydrogen adatom on metal doped α -Zr (0 0 0 1) surfaces in a vacuum and an implicit solvation environment



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ABSTRACT

First-principles calculations have been carried out to investigate the adsorption of a hydrogen adatom on 24 metal doped α -Zr (0 0 0 1) surfaces in both a vacuum and an implicit solvation environment. The dopant are the elements in the 4th and 5th periods in the periodic table. Doping elements at the tail of the 4th and 5th periods can significantly reduce the hydrogen pickup in a vacuum environment. A weighted *d*-band center theory is used to analyze the doping effect. On the other hand, the hydrogen adsorption energies in water are relatively lower for all doped slabs and the surface adsorption of hydrogen adatom is stronger than that in a vacuum environment, especially, for the slabs with doping elements at the tail of the 4th and 5th periods. In the solvation environment, electronegativity difference affects the adsorption. Doping elements Ag, Ga, Ge, Sn, and Sb can reduce the hydrogen pickup in vacuum, while Ag and Cu can reduce the hydrogen pickup of the zirconium alloys in solvent environment.

1. Introduction

During the in-pile operation, the hydrogen is released by corrosion of zirconium alloys. Hydrogen degradation happens once the hydrogen generated by the corrosion is beyond the solubility in the substrate α -Zr [1]. Hydrogen degradation is important for the mechanical properties for the cladding materials in the nuclear power plants [1,2]. Numerous experimental studies have been carried out to evaluate the hydrogen pickup for material screening [3–5]. The hydrogen pickup fraction is defined as the ratio of the hydrogen adsorbed by the metal over the total amount of hydrogen generated during corrosion reaction [6]. It has been demonstrated that this parameter is closely related to the alloying elements, the type and proportion of intermetallic precipitates, microchemistry and the corrosion conditions [5,7,8]. For instance, although the concentration of certain alloying element is tiny, the hydrogen pickup can be lowered dramatically. For example, Ni is not good for hydrogen pickup because intermetallic precipitates form and they facilitate the hydrogen pickup [7]. In addition, it was documented that the hydrogen uptake fraction differs in different stages of the waterside corrosion [9]. Because passive oxide layer forms on the cladding, the oxidation layer may affect the hydrogen pickup. Doping elements in the oxidation layer may also affect the diffusion of the hydrogen atom

[8,10]. During the stage of the oxidation layer growth, the compact passive film may crack and the zirconium alloy surfaces are exposed in the water. At this time, hydrogen adatom may be adsorbed on the zirconium surfaces [6].

Although experimental work can help engineer to design advanced zirconium alloys with a lower hydrogen pickup, a fundamental understanding of the interaction between the hydrogen adatom and the zirconium substrate is not clear. Without this knowledge, large amount of material screening experimental works are expensive and time consuming. Computational materials studies can help us investigate the material properties and optimize the material design process. For instance, the water adsorption and dissociation on transition metal doped zirconium surface, and the formation of various zirconium hydrides are well described using first-principles studies [11,12].

In this study, surface doping effects on hydrogen adsorption on α -Zr (0 0 0 1) surfaces are studied with first-principles calculations. The Zr (0 0 0 1) surface is doped with the elements in the 4th and 5th periods of the periodic table. The calculations are carried out in both a vacuum and an implicit solvation environment. The continuum solvation model is an effective method to simulate water environment. The interface of a Li_3OCl -cathode is studied with this model in solvation environment [13]. Moreover, this method is particularly useful in a heterogeneous

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electrochemical catalysis study, which mostly occurs in a solvated environment. For example, the oxidation of methanol on a Pt (111) surface, the oxygen evolution reaction on a IrO₂ (110) surface, the CO₂ electroreduction on a doped tin oxide surface, and perovskite CH₂NH₃PbX₃ (X = Br, I) surface study [14–17].

2. Computational methods

2.1. Computational detail

The ground state energies of the adsorption systems are calculated with the density functional theory (DFT) calculations, which are performed with the Vienna ab initio simulation package (VASP) code [18]. The projected augmented wave (PAW) method is used to describe the wave functions near the core region [19]. The exchange correlation functional within the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) is performed in our calculations [20]. The cutoff of the plane-wave kinetic energy is 400 eV. The integration over the Brillouin zone is performed using a 21 × 21 × 21 MonkhorstPack *k*-point mesh for the calculations of a zirconium unit cell, and a 3 × 3 × 1 *k*-point mesh for the slab calculations [21]. For the electronic relaxation calculations, the energy convergence criterion is 10^{−4} eV, whereas in the ionic relaxations, the stopping criterion for the Hellmann–Feynman force minimization is 0.05 eV/Å. Spin polarization is used in all calculations, and all atoms are free to relax. The chemical adsorption energy of a hydrogen adatom on a metal atom doped zirconium (0 0 0 1) surfaces is defined as:

$$E_{\text{ad}} = E_{\text{H/surf}} - E_{\text{surf}} - \frac{1}{2}E_{\text{H}_2} \quad (1)$$

Here, $E_{\text{H/surf}}$ is the total energy of a zirconium slab with a hydrogen adatom on the (0 0 0 1) surface; E_{surf} is the system energy of a clean zirconium slab; and E_{H_2} is the energy of a hydrogen molecule. Charge transfer between the hydrogen adatom and the neighboring surface atoms is calculated, and the atomic partial charges are computed using the decomposition scheme proposed by Bader [22]. A 5 × 5 × 1 *k*-point mesh centered at Γ point and the Gaussian smearing method with the smearing width of 0.1 eV are used to calculate the density of state (DOS) of the doped zirconium surfaces.

The solvation effect is evaluated using an implicit solvation model developed by Mathew and Hennig [23,24] which is implemented into VASP code. The relative permittivity of water background is set as $\epsilon_b = 80$ and the cutoff charge density is $\rho_{\text{cut}} = 0.0025 \text{ \AA}^{-3}$. The cavitation energies are calculated using a surface tension parameter of 0.525 meV/Å and the width of the dielectric cavity of 0.6 Å.

2.2. Computational models

The optimized lattice parameters of α -Zr are $a = 3.235 \text{ \AA}$, and $c = 5.159 \text{ \AA}$, which are close to the experiment data ($a = 3.231 \text{ \AA}$, $c = 5.148 \text{ \AA}$ [25]). It also agrees with computational results calculated by Glazoff et al. well [26].

A super cell composed of 3 × 3 unit cells with six atomic layers of metal atoms is used to simulate the hydrogen adatom adsorption on a zirconium (0 0 0 1) surface. The surface energy converge test show that a six atomic layer slab is sufficiently to simulate surface adsorption. A vacuum layer on the top of the (0 0 0 1) surface is used to eliminate the interaction between the neighbor slabs since the periodic boundary condition is applied. The thickness of the vacuum layer is 15 Å. In order to study the hydrogen adsorption on an α -Zr (0 0 0 1) surface, a hydrogen adatom is located slightly above the surface ($\approx 1.7 \text{ \AA}$). Four possible adsorption sites are considered for a hydrogen adsorption process, the top site of a surface atom (top), the two-fold bridge site between two neighboring surface atoms (bri), the three-fold hcp and the fcc hollow sites around a surface atom (see Fig. 1). For the surface doping effect calculations, the central zirconium atom at the top atom

layer of the super cell is substituted by a transition metal atom, which is in the 4th or 5th period of the periodic table.

To further validate the accuracy of the aforementioned parameters chosen in this work, the surface energy of an α -Zr (0 0 0 1) surface, and the binding energy and vibrational frequency of H₂ molecule are calculated. Without considering the zero-point energy, the surface energy is defined as:

$$E_{\text{surf}} = \frac{E_{\text{surf}} - E_{\text{bulk}}}{2A_{\text{surf}}} \quad (2)$$

where E_{surf} is the surface energy, E_{bulk} is the bulk energy of a bulk supercell with equivalent number of atoms, and A_{surf} is the surface area of the slab. The calculated surface energy of the zirconium (0 0 0 1) is 1.58 J/m², corresponding to 0.896 eV/atom, which agrees with both the experiments (0.80–1.05 eV/atom) and computational results (0.901 and 0.88 eV/atom) well [27–29]. The binding energy of a H₂ molecule is 4.55 eV, and the vibrational frequency is $\omega = 4269 \text{ cm}^{-1}$, corresponding to a zero point energy of 0.266 eV. The results agree with experimental and computational data well [30,31].

3. Results and discussion

3.1. Hydrogen adatom adsorption on a Zr (0 0 0 1) surface in vacuum

3.1.1. Adsorption energies

The adsorption energies of a hydrogen adatom on transition metal doped Zr (0 0 0 1) surfaces in a vacuum environment are shown in Fig. 2. A hydrogen adatom is adsorbed on four possible adsorption sites of a Zr (0 0 0 1) surface. After relaxation, the hydrogen adatom may be repelled from the initial site and migrate to a second nearest neighbor site. For example, in the Fig. 3(a), the hydrogen adatom adsorbed on the Ag doped Zr (0 0 0 1) surface migrates to the second nearest neighbor hcp site after relaxation. Although after relaxation, the hydrogen adatom can stay on the top of the Ag atom, the adsorption energy is positive and it is not energetic favorable. This phenomenon has been reported by Nie et al. as well [12]. Although the adsorbed hydrogen adatom still stay around the doping defect, the surface distortion happens. For example, the adsorbed hydrogen pushes the Fe atom inward to the bulk, and the Fe moves close to the hydrogen adatom (see Fig. 3(b)) after relaxation. It indicates that the doping element of Fe shows high affinity towards the hydrogen adatom. The adsorption energies and the bond lengths of a hydrogen adatom on a Ag or Fe doped Zr slab in both vacuum and water environment are listed in the Table 1.

The hcp and the fcc hollow sites on a pristine Zr (0 0 0 1) surface are the energetically favorable sites for a hydrogen adatom, and the corresponding adsorption energies are −0.99 eV at the fcc site and −1.05 eV at the hcp site, respectively. The calculated results agree well with the values of −0.96 eV and −1.02 eV reported by Peng Zhang et al. [11]. On the other hand, the top site on a Zr (0 0 0 1) surface is the least stable adsorption position for a hydrogen adatom. Although the bridge position is also considered as an initial adsorption site, it is not a stable configuration. As a result, the adsorption energy of a hydrogen atom on the bridge site is not shown in Fig. 2. Suppose a hydrogen adatom is adsorbed on a doped zirconium slab in vacuum, a geometrical change happens after relaxation. In our calculations, the hydrogen adsorption does not change the configurations of the doped zirconium slabs too much and the hydrogen adatom is still around the initial position. The dopants of these slabs include V, Cr, Cu, Zn, Ga, Y, Zr, Nb, Mo, and Pd. In the second category, after relaxation the geometries of the slabs do not change significantly, but the hydrogen adatom can only stay on the top site or it migrates to second nearest neighbor site. The dopants of these slabs include Ge, Ag, Cd, In, Sn, and Sb. On the other hand, for Mn, Fe, Co, Ni, Ru, and Rh doped zirconium slabs, the surface distortion happens around the adsorption site near the doping elements.

Transition metal atoms are used to substitute a surface zirconium

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