Adsorption of H on Cs/W(110): Impact of H on the Stability of Cs on the Surface

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We studied the adsorption of H on Cs/W(110) by performing density functional theory (DFT) based total energy calculations to determine the influence of H on Cs stability on the surface. For reference, we also independently examined the adsorption of H and Cs on clean W(110). We found that the adsorption energies of both H and Cs decrease in the presence of the other. H adsorbs more strongly in H/W(110) as compared to the coadsorbed system H/Cs/W(110). We observe the same trend for Cs adsorption in Cs/W(110) and H/Cs/W(110) systems. Due to the greater electronegativity of H as compared to Cs, increasing the H coverage further weakens Cs adsorption on the W surface. The results suggest that the presence of H could lead to the desorption of Cs from the surface and thus, it is necessary to reevaluate the designs of Cs/W systems used in negative hydrogen production applications.

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I. INTRODUCTION

Negative hydrogen ions (H\(^-\)) are essential as sources for magnetic confinement in fusion research [1] and as particle sources in high energy accelerators [2]. Negative hydrogen ions can be produced via scattering particles (ions or atoms) from the surface (surface production) [3]. One would expect low work function surfaces would facilitate charge transfer from the surface to the impinging particle. Low work function surfaces may be realized via the adsorption/deposition of Cs atoms and/or other alkali elements on metal surfaces. The electropositive nature of the alkali metal adsorbrates results in an induced surface dipole moment, which in turn results in a low work function material [4]. Several notable previous works, both experimental and theoretical, have reported metal surface work function modifications with alkali metal adsorption [5–11].

As expected, introduction of Cs resulted in increased negative ion yield [2, 12]. However, frequent injection of Cs can lead to Cs leakage [13], which causes voltage breakdown and damages the acceleration system. Cs layers may also form at other parts of the ion source during operation [2, 14]. Cs may deplete from ion sources of high energy accelerators [15], and from cesiated systems with Ar added into the hydrogen discharge [16]. The removal of adsorbed Cs from metal surfaces, e.g., Mo surfaces, has been attributed to the existence of impurities such as O\(^+\) [15]. This indicates that the presence of impurities influences the stability of the adsorbed Cs atoms. To our knowledge, however, there is no conducted study that specifically investigates the effect of H on the stability of Cs on metal surfaces. We see the importance of such investigation since H atoms are the key species in hydrogen negative ion formation and due to the role of Cs in work function lowering. Here, to clarify the mechanism behind how H influences the stability of adsorbed Cs atoms on metal surfaces, we consider H adsorption on Cs/W(110).

The International Thermonuclear Experimental Reactor (ITER) uses W as the first wall and it has similar characteristics as the Mo used in neutral beam injectors.

To study how the H affects the stability of Cs adsorption on W(110), we performed density functional theory (DFT) based total energy calculations. For reference, we also independently examined the adsorption of H and Cs on clean W(110). Our results show that the adsorption energies of both H and Cs decrease in the presence of the other. H adsorbs more strongly on H/W(110) as compared to the coadsorbed system H/Cs/W(110). We observe the same trend for Cs/W(110) as compared to...
H/Cs/W(110). Due to the greater electronegativity of H as compared to Cs, increasing the H coverage further weakens Cs adsorption on the W surface. Based from our results, we suggest that it is necessary to reconsider designs of Cs/W with better Cs stability and can facilitate negative hydrogen ion production.

II. COMPUTATIONAL DETAILS

We performed density functional theory (DFT) based total energy calculations \cite{17,18}, using projector augmented wave (PAW) method to describe the ionic core pseudopotentials \cite{19}, the Perdew-Burke-Ernzerhof (PBE) functional \cite{20} to approximate the exchange correlation energy, and plane waves with energy cutoff of 600 eV to solve the corresponding Kohn-Sham equations. We determined the ground-state geometries of the bulk and surfaces by fixing the W in the bottom two layers in their bulk positions, and allowing the remaining atoms to relax, requiring an energy convergence criterion of $10^{-5}$ eV, and the maximum force acting on each atom to be below 0.01 eV/Å. The calculated optimized bulk lattice parameters for W is $a = 3.17$ Å (cf., Refs. \cite{21,22,23}). To model W(110), we used a periodic slab of four W atomic layers, separated by 25 Å of vacuum. To simulate 0.22 ML Cs coverage (optimum Cs coverage yielding the minimum work function for Cs/W(110) \cite{6}), we used $(3 \times 3)$ surface units cells with $(6 \times 6 \times 1)$ gamma centered k-point meshes \cite{24}. We then investigated H adsorption (0.11 ML). We determined the adsorption energies of H atoms with respect to the total energy of the clean surface and half of the total energy of an isolated H$_2$. A more negative adsorption energy value implies stronger adsorption. We would like to note that aside from backscattering, desorption of adsorbed H from cesiated surface likewise produces negative ions \cite{25}. Thus, our present model allows us to determine the effect of adsorbed H on the stability of Cs and agrees with the actual physical systems. We also performed Bader charge analysis to quantify the amount of charge in the atoms comprising the systems \cite{26,27}.

III. RESULTS AND DISCUSSION

A. Cs on W(110)

Figure 1 shows the structure of W(110) and 0.22 ML of Cs on W(110) surfaces. The height of the Cs atoms from the topmost layer W is ~$3.35$ Å, which is larger than the interlayer distance of the topmost and the next layers of the W surface with value of ~$2.17$ Å. The large difference in the distances is attributed to the larger atomic radius of Cs than the W and is evident from the lattice constants of bulk Cu and W with values of 6.05 Å and 3.16 Å, respectively \cite{21}. We obtained ~$1.84$ eV as the average adsorption energy of Cs atoms on the surface and are adsorbed on the long bridge symmetry site. We found in our previous study that the 0.22 ML Cs coverage on W(110) yields the minimum work function, 1.42 eV \cite{6}. Increasing the Cs coverage to 0.33 ML, the saturation coverage of Cs on W(110) for monolayer structure, will result to a higher work function (~$1.80$ eV). To basically understand the interaction of the Cs atoms and the W surface, we plotted in Figure 2 the density of states (DOS) of adsorbed Cs and surface W atoms. The plot generally shows the hybridization of the states of Cs and W atoms, which characterizes the interaction between Cs and surface W atoms. This agrees with the results of Chou et al., in which they suggested that the differences in the adsorption strength of Cs on different metals is due to electronic effects and is likewise supported by the analyzed DOS plots \cite{4}.

| Adsorption site     | Adsorption energy (eV) | Charge gained by H (e) |
|---------------------|------------------------|------------------------|
| Long bridge (lb)    | -0.53                  | 0.396                  |
| Short bridge (sb)   | -0.69                  | 0.390                  |
| Threefold (3f)      | -0.76                  | 0.427                  |
| Top (t)             | -0.11                  | 0.298                  |

TABLE I. Adsorption energy of and charge gained by the hydrogen atom on W(110).
TABLE II. Adsorption energy of and charge gained by the hydrogen atom on Cs/W(110). The average adsorption energy of Cs is also indicated.

| Adsorption site      | H adsorption energy (eV) | Cs average adsorption energy (eV) | Charge gained by H (e) |
|----------------------|--------------------------|----------------------------------|-----------------------|
| Long bridge1 (lb₁)   | -0.45                    | -1.69                            | 0.436                 |
| Long bridge2 (lb₂)   | -                        | -                                | -                     |
| Short bridge1 (sb₁)  | -0.62                    | -1.78                            | 0.446                 |
| Short bridge2 (sb₂)  | -0.58                    | -1.76                            | 0.476                 |
| Threefold1 (3f₁)     | -0.68                    | -1.81                            | 0.460                 |
| Threefold2 (3f₂)     | -0.64                    | -1.79                            | 0.479                 |
| Top1 (t₁)            | -0.14                    | -1.54                            | 0.451                 |
| Top2 (t₂)            | -0.38                    | -1.66                            | 0.474                 |

a H relaxes to the threefold site (3f₂) after optimization.

FIG. 3. Adsorption structures of H on (a) threefold and (b) top sites of W(110), and on (c) threefold and (d) top sites of Cs/W(110). The figures in the upper (lower) panel illustrate the top (side) views of the surfaces.

B. H on W(110) and Cs/W(110)

The adsorption sites of the H atom on W(110) and Cs/W(110) surface is also illustrated in Fig. 1. The adsorption energy and the charge gained by the H atom on W(110) and Cs/W(110) are listed in Tables I and II, respectively. On W(110), H is most stable on the threefold site with adsorption energy of -0.76 eV. This result is in good agreement with a previous DFT work, in which, the reported adsorption energy of H on threefold site of W(110) is -0.75 eV [28]. On the other hand, we obtained lower adsorption energies of H on Cs/W(110) surface as compared to the case of W(110). For the cesiated surface, we considered adsorption sites that are relatively far and near the positions of the Cs, respectively labeled with subscripts 1 and 2 in Fig. 1(b). Table II shows that the most stable H adsorption remains at the threefold site (3f₁), with a corresponding adsorption energy of -0.68 eV. H adsorption energies at the 3f₁ and 3f₂ threefold sites differ by ~0.04 eV, and also for H adsorption at the sb₁ and sb₂ short bridge sites. We did not obtain stable H adsorption on the other long bridge sites (lb₃) located nearer to the Cs. Instead, the H relaxes to the threefold site (3f₂) after optimization. H adsorption energies at the t₁ and t₂ top sites differ by ~0.24 eV with t₂ (located immediately between two Cs atoms) being more stable. Lastly, the charge gained by the H atom is higher when Cs are present on the surface than on clean W(110), which supports the observed high ionization yield of scattered H on cesiated surface.

We first analyzed the geometric properties of H-W(110) and H-Cs/W(110) systems to primarily determine the influence of Cs atoms on the H atom. Figures 3(a, b) and 3(c, d) show the comparison of the adsorption structures of H on W(110) and on Cs/W(110) for threefold and top site adsorptions, respectively. We chose the threefold sites since these are the most stable adsorption sites of H on the surfaces. We also considered the top site adsorption because in such configuration, H is positioned exactly between the two Cs atoms. In general, we can see that the distances of H to its nearest neighbor W atoms and the height of H from the W surfaces are comparable on both cases. The geometric properties of H with reference to the W surface is not substantially modified by the presence of Cs atoms. Since the height of Cs from the W surface is relatively large and H prefers to be adsorbed near the W than Cs atoms, H will most likely assume a configuration that is similar with its adsorption structure on clean W.

We now focus on the impact of H adsorption toward the
Cs atoms on the surface. The average adsorption energy of Cs atoms is reduced when H is present on the surface as depicted in Table II. Such reduction is most evident when H atom is located near the Cs atoms, e.g., top site adsorption, in which the average adsorption energy of Cs is reduced by \( \sim 0.18 \) eV. It clearly shows that the presence of H lowers the adsorption energy of Cs on the W surface, which might contribute as well to the removal of Cs atoms from the plasma electrodes during ionization experiments. In a recent study, it is found that lower or negligible barrier accompanies the adsorption of H atom on adsorption sites that are not close to the Cs atoms of Cs/Mo system, however, the origin of such observation is not clarified in the study [29].

We illustrate in Figs. 4(a) and 4(b) the charge density difference profiles of H–Cs/W(110) system projected on H and Cs atoms, respectively. For reference, we show in Fig. 4(c) the charge density difference profile of clean Cs/W(110) projected on the Cs atoms. As mentioned earlier, states of Cs and W atoms hybridize to form bond. This is clearly illustrated by the electron rich (red) region in the Cs and W interface [Fig. 4(c)], which can be inferred as shared by both the Cs and W atoms. The adsorption of H, on the other hand, is characterized by charge transfer process. H gains charge from the neighboring metal atoms. Figure 4(a, b) shows the electron rich region around the H atom and an electron depleted (blue) region between the H atom and the metal (both W and Cs) atoms. Thus, the higher charge gain of H in the presence of Cs can be attributed from the fact that both Cs and W donate charge to the H. The ability of H to accept charge from the metal atoms is supported by its higher electronegativity than that of Cs and W [30]. The charge transfer from the metal atoms to H weakens the interaction between the Cs and W surface, which leads to the reduced adsorption energy of Cs with co-adsorbed H. On the other hand, the adsorption of H on cesiated tungsten is weaker than on clean tungsten surface because W accommodates both the Cs and H atoms. These claims are consistent with the lower adsorption energies both of H and Cs when these atoms are positioned near each other (Table II). To further verify the influence of H on the Cs atoms, we calculated the adsorption of 1.0 ML of H (on the threefold sites) on the Cs/W(110) surface. Here, we found that the average adsorption energy of H is \(-0.61\) eV and is slightly lower than the adsorption energy at low coverage, \(-0.68\) eV. With higher H coverage, the average adsorption energy of Cs is greatly reduced to \(-1.30\) eV. For such H coverage, all the W surface atoms participate in the charge transfer process which results to much lower Cs adsorption energy. In addition, the height of the Cs from the W surface is increased to \(\sim 3.60\) Å (from an initial height of \(\sim 3.35\) Å) which further proves that the presence of H atoms weakens the adsorption of Cs atoms on W(110) surface.

IV. CONCLUSION

We investigated the adsorption of H atom on W(110) and on Cs/W(110) surface by performing density functional theory (DFT) based total energy calculations to determine the influence of adsorbed H atoms on the stability of Cs on metal surface. Our results show that the average adsorption energy of Cs decreases when H is adsorbed on the surface. Weaker adsorption energy also characterizes the adsorption of H on Cs/W(110), as compared to its adsorption on clean W(110) surface. Charge density difference profiles reveal that the W atoms interact both with H and Cs which leads to a weaker interaction between H and W and between Cs and W. Our study suggests that there is a need to reconsider the design of surfaces for production of negative hydrogen ion via the surface production method. While Cs/metal systems are usually employed for such application, it is important that the stability of the system be carefully examined. It is clear from our results and from previous works [2, 14–16] that the presence of other adsorbates (including H) and the plasma environment weaken the stability of Cs, which can lead to the removal of Cs from metal surfaces. To protect Cs from the impinging H species and other particles, we recommend that Cs implanted in W surfaces, alloys of WC, and incorporation of Cs in W based systems (e.g., W carbide and W oxide) be tested as possible designs to enhance the adsorption of Cs. Further investigations on the stability of Cs in these systems and on their performance for negative hydrogen ion production are needed.

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