Elucidating the Initial Steps in $\alpha$-Uranium Hydriding Using First-Principles Calculations

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1. INTRODUCTION

Uranium is a unique element that can be used in the energy industry as a nuclear fuel to generate electricity and by the military to power submarines and for weaponry. However, the fundamental molecular-level mechanism of this process remains unknown. In this work, starting from pristine $\alpha$-U bulk and surfaces, we present a systematic investigation of possible mechanisms for the formation of metal hydride. Specifically, we address this problem by examining the individual steps of hydrogen embrittlement, including surface adsorption, subsurface absorption, and the interlayer diffusion of atomic hydrogen. Furthermore, by examining these processes across different facets, we highlight the importance of both (1) hydrogen monolayer coverage and (2) applied tensile strain on hydriding kinetics. Taken together, by studying previously overlooked phenomena, this study provides foundational insights into the initial steps of this overall complex process. We anticipate that this work will guide near-term future development of multiscale kinetic models for uranium hydriding and subsequently identify potential strategies to mitigate this undesired process.

ABSTRACT: Hydrogen embrittlement of uranium, which arises due to the formation of a structurally weak pyrophoric hydride, poses a major safety risk in material applications. Previous experiments have shown that hydriding begins on the top or near the surface (i.e., subsurface) of $\alpha$-uranium. However, the fundamental molecular-level mechanism of this process remains unknown. In this work, starting from pristine $\alpha$-U bulk and surfaces, we present a systematic investigation of possible mechanisms for the formation of metal hydride. Specifically, we address this problem by examining the individual steps of hydrogen embrittlement, including surface adsorption, subsurface absorption, and the interlayer diffusion of atomic hydrogen. Furthermore, by examining these processes across different facets, we highlight the importance of both (1) hydrogen monolayer coverage and (2) applied tensile strain on hydriding kinetics. Taken together, by studying previously overlooked phenomena, this study provides foundational insights into the initial steps of this overall complex process. We anticipate that this work will guide near-term future development of multiscale kinetic models for uranium hydriding and subsequently identify potential strategies to mitigate this undesired process.
surface is typically covered with a protective oxide layer when exposed to air, which acts as a barrier to hydrogen reactivity, including diffusion and dissociation, and introduces a factor of unpredictability into the observed hydriding induction times. These studies would greatly benefit from atomic-level detail about hydrogen–uranium surface reactions, nucleation, and growth parameters as hydrided layers begin to form.

Density functional theory (DFT) is a well-established computational approach in material science, physics, and chemistry for the prediction of physical and chemical properties. DFT has been used to study numerous metal–hydrogen systems across the periodic table, including palladium alloys, titanium, and many other systems. It has also been used to compute bulk absorption in plutonium as well as hydrogen ML coverage on its low-energy facets. Several previous studies have probed the initial interactions of α-U and hydrogen in the dilute limit (i.e., a single hydrogen atom per surface) using DFT. For example, some results exist regarding surface energies, single atom/molecule geometries, point defect formation energies in the bulk, and adsorption energies on the (001) surface (generally considered to be the most stable). While these studies provide useful information about the very first steps of the hydriding process (including H₂ dissociation), the effects of strain, concentration and partial pressure of hydrogen, and ML coverage remain entirely unknown. Hence, our effort is the most in-depth ab initio study of U–H interactions as well as the uranium hydriding phase diagram that we know of to date.

In this paper, we greatly expand upon these results by using DFT to further examine possible mechanisms for uranium hydriding, including bulk effects, the presence of multiple surfaces, and a wide range of hydrogen concentrations. First, we perform a thorough analysis of DFT exchange–correlation functionals and theoretical approaches in order to determine an appropriate computational protocol that reproduces experimentally known bulk and surface properties. Hydrogen embrittlement and the phase transformation to α/β-UHₓ involve both changes in the chemical composition and volumetric expansion of the lattice. Consequently, we investigate the process of uranium hydriding from two perspectives: (1) from the formation of hydrogen ML coverage and (2) as a function of applied tensile load on the α-U lattice.

We believe that both of these mechanisms could play significant roles in hydrogen embrittlement, and we quantify the relative importance of different surface adsorption sites and facets in the process.

2. COMPUTATIONAL DETAILS

DFT calculations were performed using the Vienna ab initio simulation package code (VASP). The projector augmented wave (PAW) pseudopotentials for U provided in VASP include 6s²6p⁶6f¹⁴⁷⁷s⁴ as valence electrons. Fourth-order Methfessel–Paxton smearing was used with a value of 0.2 eV for all optimization calculations in order to ensure energy convergence without dependence on the electronic smearing temperature. In our initial calculations, we examined the following exchange–correlation functionals: Perdew–Burke–Ernzerhof (PBE), dispersion-corrected PBE (PBE_D3BJ, RPBE_D3BJ), and PBEsol and SCAN, which were developed specifically for solids and solid surfaces. The energy cutoff for the planewave basis set for all of our calculations was set to 500 eV based on convergence tests. Structural relaxations were performed until forces on each atom were less than 0.01 eV/Å. A k-point mesh of 14 × 7 × 8 generated by the MonkhorstPack method for integration over the Brillouin zone was used for the primitive bulk unit cell optimization.

The alpha phase of uranium has a face-centered orthorhombic structure with a Cm̅Cm̅ space group, as shown in Figure 1. To investigate the interaction between atomic hydrogen and α-U surfaces, a slab model with at least a six-layer thickness was employed, in which the bottom two layers were constrained to simulate the bulk environment, while the rest were allowed to relax in their equilibrium positions. A vacuum layer of 15 Å between two adjacent slab surfaces was found to be adequate for all relevant calculations.

The surface adsorption and subsurface absorption behavior of hydrogen was modeled using a (2 × 1) surface unit cell with 6–10 layers depending on the facet (between 24 and 40 U atoms), while the bulk absorption was modeled using a 4 × 2 × 2 supercell (64 U atoms). For a converged, clean slab, the surface energy was calculated using the following formula

\[ E_{\text{surf}} = \frac{E_{\text{slab}} - N_{\text{U}} E_{\text{bulk}}}{2A} \]  

(1)
where $E_{\text{slab}}$ is the total energy of the N-atom slab, $E_{\text{bulk}}$ is the bulk energy per atom, $\alpha$ is the area of the surface, and $N$ is the number of atoms in the surface slab. $E_{\text{bulk}}$ is approximated using the Fiorentini and Methfessel\(^{25}\) approach of a linear fit of DFT energies from slabs of different thicknesses.

The adsorption energy of one H atom on an $\alpha$-U surface and the absorption energy into a subsurface site were determined using the following expression:

$$E_{\text{ads/abs}} = E_{(U/H)} - E_{(U)} - 1/2E_{(H_2)}$$

where $E_{(U/H)}$ is the total energy of the optimized hydrogen + slab system, $E_{(U)}$ is the total energy of the clean slab, and $E_{(H_2)}$ is the total energy of the optimized isolated $H_2$ molecule. A negative adsorption energy corresponds to a stable adsorbate—surface system.

3. RESULTS AND DISCUSSION

3.1. Functional Comparison.

3.1.1. Lattice Parameters.

Before we investigate uranium surface chemistry, we first perform a benchmark comparison study of the equilibrium lattice parameters with various exchange—correlation functionals with experimental values. As shown in Table 1, all exchange—correlation functionals used here underestimate the experimentally reported lattice constants. However, these deviations are relatively small (less than 3.97%). Even though PBEsol is designed to improve upon PBE for equilibrium lattice parameters, we also performed an exchange—correlation functional comparison study by computing surface energies (Table 2). Here, we chose the (001) surface as this is the most stable $\alpha$-U facet. The experimental surface energy of $\alpha$-U is 1.828 J/m\(^2\); however, this value corresponds to an isotropic crystalline structure of the metal or an average value of different surfaces.\(^{15}\) Since the (001) facet has the lowest energy, it would be the most abundant surface in the uranium crystalline material. As presented in Table 2, the descending order of the surface energy for various functionals is RPBE_D3BJ > PBE_D3BJ > PBEsol > PBE > SCAN. The experimental surface energy is in close proximity to the results determined from PBE and SCAN, while estimates by other functionals are much higher.

Van der Waals (vdW) interactions are generally significant for surface properties, and their inclusion in DFT models remains an area of active research.\(^{15}\) PBE generally neglects most of the vdW interactions, while SCAN incorporates intermediate-range vdW, and D3 functionals include even long-range dispersion effects. Remarkably, these dispersion effects are of less importance in estimating bulk and surface properties in $\alpha$-U. As mentioned, the closest agreement in estimating the surface energies was achieved by PBE and SCAN. SCAN is considered a more advanced functional due to the inclusion of all 17 known exact constraints that a meta-
GGA can satisfy. However, we only notice slight improvements in results calculated by SCAN over PBE.

In addition to surface energies, we performed a similar comparison study for estimating atomic hydrogen adsorption energies on the most stable (001) α-U surface (Figure 2). As shown, five possible unique adsorption sites (denoted as top, hollow1, hollow2, longbridge, and shortbridge) were considered. For all cases, the H atom is unable to remain stable at the top, longbridge, or shortbridge sites, relocating to a more stable hollow site nearby. This indicates that there are only two preferred adsorption sites on the (001) surface for a single hydrogen adsorption: hollow1 and hollow2. Similar results are observed in nitrogen–uranium and oxygen–uranium systems. In addition, all functionals used here indicate that the hollow2 site is slightly more energetically favorable (∼0.06 eV) compared to hollow1. Table 2 also shows minimal differences between functionals, with a relatively small energetic spread of ∼0.08 eV for all approaches due, in part, to the various representations of vdW interactions. We note that quantum nuclear vibrational zero-point energies (ZPEs) can be significant for low-Z elements such as hydrogen. We observe that the ZPE occurs as a systematic correction of ∼0.16 eV for all functionals studied here. We discuss the effects of the ZPE further regarding reaction energies and kinetics (Section 3.4) and our computed ML coverage phase diagrams (Section 3.4).

Overall, we have computed the lattice constants, surface energies, and atomic hydrogen adsorption energies on the (001) facet. We have compared experimentally determined results to those calculated by various exchange–correlation functional approaches. Given the correct ordering and reasonably small differences in adsorption energies, surface energies, and lattice constant results, PBE was our functional of choice for the rest of our studies.

Surface energies and adsorptions have been shown to be relatively insensitive to the value of the Hubbard U correction in actinides. Similar results have been seen with materials containing lower-Z metals, where inclusion of GGA + U had a minimal effect on surface energy ordering. In addition, uranium phases are known to exhibit magnetic moments at their surface, which can affect surface adsorption energies. In order to assess these effects on α-U surface properties and hydrogen adsorption, we have chosen to perform a bounding study using PBE on the faceted (012) and (102) surfaces, which are the two highest energy/most reactive surfaces studied in our work (see Section 3.3 for further discussion). Here, we compute surface energies and hydrogen adsorption energies for the lowest energy site (i.e., the stepped site) using GGA + U and spin polarization separately in order to independently quantify the effect of each treatment. This approach places an upper bound on these effects since these surfaces likely exhibit the largest surface magnetization or other sensitivities due to the choice of the DFT method.

In the case of our GGA + U calculations, we find that the resulting surface energies experience small changes for each facet (Table 3), with the (012) surface energy shifting to a lower value by ∼4% (2.15 vs 2.07 J/m² for GGA + U) and the (102) surface energy shifting upward by ∼5% (1.92 vs 2.02 J/m² for GGA + U). Additionally, we find that this shift results in a fairly small change in hydrogen adsorption energy (Table 4), where adsorption is enhanced (e.g., more negative) by 0.13 eV on the (012) facet and is diminished (more positive) by 0.02 eV on the (102) facet. We note that these deviations are similar in magnitude to the spread of adsorption energy results due to the choice of the exchange–correlation functional, shown in Table 2. Hence, we have opted not to include GGA + U corrections, given that these deviations represent a relatively small upper bound on our calculations.

Regarding spin polarization, we observe significant spin moments on the surface uranium atoms, with a value of ∼2 for each surface (Table 3). However, the effect on the computed surface energies is relatively small, with the (012) surface energy shifting to a lower value by ∼5% (down to 2.05 J/m²) and the (102) surface energy shifting higher by ∼6% (up to 2.03 J/m²). Similar to GGA + U, the effect on hydrogen adsorption energies is relatively small (Table 4). We find that (012) adsorption is diminished by 0.09 eV and that (102) adsorption is diminished by 0.07 eV. As a result, we find no substantial loss in accuracy due to excluding spin polarization from the results presented here as well. A systematic investigation to further quantify GGA + U and spin polarization effects on uranium surface properties is the subject of future work.

3.2. Absorption into the α-U (001) First Subsurface Layer. Upon molecular dissociation, atomic hydrogen tends to bind in thermodynamically favored surface adsorption sites.
This can be followed by diffusion of hydrogen from the surface to the subsurface, which could also play a substantial part in the hydrogen embrittlement process. We now calculate the energetic parameters of hydrogen absorption into the first subsurface layer. In this section, we present results for the (001) facet, while results (for the most stable site) for all other surfaces of interest are presented in Table S2 (Supporting Information).

Figure 3 shows the typical interstitial sites for the (001) surface: tetrahedral (Tet), square-pyramidal (Sqpy), and octahedral (Oct). Due to the low symmetry of the α-U surface, there are one Oct and two types of Tet and Sqpy sites between the top and the first subsurface layers. Tet1 has three surface and one subsurface uranium nearest neighbors, while Tet2 is surrounded by one surface and three subsurface U atoms (Figure 3a,b). Sqpy1 has three surface and two subsurface U nearest neighbors, while Sqpy2 has two surface and three subsurface U atoms (Figure 3c,d). Oct has three surface and three subsurface U atom nearest neighbors (Figure 3e).

The subsurface interstitial/absorption energies for each unique site are calculated using eq 2. The absorption energies, site type, the distances between the absorbed hydrogen and top surface layer are listed in Table 5. All of the subsurface absorptions in the first sublayer are found to be endothermic. The subsurface absorption at the Tet1 site is found to be the most favorable (0.16 eV), followed by Sqpy1 (0.25 eV), Sqpy2 (0.32 eV), and Tet2 (0.49 eV). In fact, the Tet1 value is almost half of the absorption energy of 0.32 eV at the tetrahedral interstitial site in the bulk (as per our own calculations). The first-layer subsurface absorption at the Oct site was found to be unstable as the hydrogen atom prefers to migrate to the more stable Sqpy1 site during geometry optimization. We notice a trend of sites closer to the surface having lower energetics, in line with lower \( d_{H-\text{surf}} \) values, as shown in Table 5.

We perform similar analysis of subsurface absorption on other low-index facets, and the most favorable energetic sites are shown in Table S2 (Supporting Information). In general, we find that these are either of Tet or Sqpy geometry, and absorption energy increases as hydrogen penetrates deeper within the lattice. Regardless of the surface, single hydrogen absorption into a defect-free α-U surface is an endothermic process for all facets studied here.

3.3. Effect of the Tensile Load on Surface Adsorption, Subsurface Absorption, and Diffusion. Due to the substantial lattice expansion of α/β-UH\(_3\) compared to that of α-U, there is likely a significant tensile strain of the α-U lattice as more hydrogen diffuses into the bulk. In this section, we investigate the surface adsorption and subsurface absorption properties as a function of applied tensile load on an α-U surface supercell of 6–10 layer thickness (with the bottom 2 layers fixed). Convergence studies indicated that a six-layer slab with a vacuum layer of 15 Å between the two adjacent slab surfaces is adequate for all relevant calculations. Tensile strain is applied to each facet by first applying an isotropic strain to the bulk, followed by optimization of the ion positions. We then create a surface slab for each facet and optimize its geometry while constraining the bottom two atomic layers. Interplanar distances are then computed by selecting a given surface atom and calculating the distance of the atom directly underneath.

In order to investigate thermal activation of these dilated geometries, we have computed the pressure–volume work required to create tensile loads in the bulk by fitting volumetric strain data to the Birch–Murnaghan isothermal equation of state and computing the pressure–volume work. Our results indicate that \( \sim 0.04 \text{ eV} \) is required for the lattice to expand up to 4%, which is likely thermally accessible under ambient conditions, and we use this value as an upper bound for our study here.

Figure 4a shows the surface energies for three standard terrace surfaces, (001), (010), and (100), as well as those for two kinked facets, (012), and (102), all as a function of applied tensile strain. In addition to common low-index terrace surfaces, we have analyzed a few stepped facets (Supporting Information, Figure S1). In realistic systems, surfaces are nonideal and defect-rich and contain imperfections, such as kinks, steps, or defect sites. In fact, stepped facets play a significant role in the palladium hydriding process,\(^43\) implying their potential significance in this work as well. When no strain is applied, (001) is the most stable facet relative to other surfaces. In contrast, the α-U (012) kinked facet has the highest energy and, thus, is the most unstable. When symmetric tensile strain is applied, the surface energy decreases for all facets. In fact, the volumetric expansion of the lattice causes densification along the surface normal as the interlayer distance decreases with applied load, which is compensated for with increased U–U bond distances within the same layer (Table S1 in the Supporting Information). The effective coordination number can serve as an additional descriptor for predicting surface chemistry and activation energies\(^44,45\) and could be included in subsequent works.

Table 5. Subsurface Absorption Energies and Geometric Parameters of Hydrogen Atoms under the \((2 \times 1)\) α-U (001) Surface\(^a\)

<table>
<thead>
<tr>
<th>interstitial type</th>
<th>( E_{\text{abs}} ) (eV)</th>
<th>( d_{H-\text{surf}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tet1</td>
<td>0.16</td>
<td>0.463</td>
</tr>
<tr>
<td>Tet2</td>
<td>0.49</td>
<td>1.884</td>
</tr>
<tr>
<td>Sqpy1</td>
<td>0.25</td>
<td>0.818</td>
</tr>
<tr>
<td>Sqpy2</td>
<td>0.32</td>
<td>1.379</td>
</tr>
<tr>
<td>Oct</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)\( E_{\text{abs}} \) denotes the average absorption energy to insert a H atom inside the first subsurface layer and \( d_{H-\text{surf}} \) represents the distance between the H atom and the top surface layer.

\(^43\)\( E_{\text{abs}} \) denotes the average absorption energy to insert a H atom inside the first subsurface layer and \( d_{H-\text{surf}} \) represents the distance between the H atom and the top surface layer.

\(^44\)\(^45\) The effective coordination number can serve as an additional descriptor for predicting surface chemistry and activation energies and could be included in subsequent works.

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**Figure 3.** High-symmetry interstitial sites of hydrogen atoms in the first subsurface layer of the α-U (001) surface: (a) Tet1, (b) Tet2, (c) Sqpy1, (d) Sqpy2, and (e) Oct. The top layer U atoms are labeled in blue, the second layer U atoms in yellow, and the hydrogen interstitial in red.
The effect of tensile strain on H atom surface adsorption and subsurface absorption is shown in Figure 4b–d (also Table S2 in the Supporting Information). Here, we compare the lowest surface adsorption to the lowest subsurface absorption site, as well as assess the trends for hydrogen diffusion from the most stable surface site to the nearby subsurface site. For all facets and tensile loads, hydrogen surface adsorption prefers to bind at the hollow 3-fold sites, excluding the (010) surface where the 4-fold adsorption sites are uniformly favored. On the other hand, the tetrahedral subsurface site is preferred for the (001), (012), and (102) surfaces, while square-pyramidal is favored in (010) and (100) slabs. Adsorption on the stepped facets is more energetically favorable than on terrace surfaces (Figure 4a). For example, under 0% strain, the adsorption energies for
In addition, we observe that tensile strain uniformly results in lower hydrogen surface adsorption energy (Figure 4a). Similar trends are observed in H/Pt (111) and H/Rh (111) systems and have been confirmed in phenomenological thermodynamic studies, where a tensile load leads to stronger hydrogen bonding to the surface of interest. When elastic strain is applied, two effects promote bonding between hydrogen and nearby uranium atoms. With increased tensile strain, the distances between all atoms within a surface layer also increase, which leads to a decreased bond strength. However, counteracting this effect is the simultaneous reduction of the distance between the hydrogen adsorbate and the subsurface U atoms, which then stabilizes adsorbate–surface interactions. In addition to the adsorption energy, we also notice that tensile strain has a significant effect on the subsurface absorption energy (Figure 4b). In fact, only 2% tensile strain is required for subsurface absorption to become an exothermic process.

As shown in Figure 4c, the energy difference (ΔE) between surface adsorption and subsurface absorption energies decreases as tensile strain increases, which means that lattice expansion can facilitate the formation of hydride. This effect is enhanced in terrace surfaces, for example, (001), (010), (100), compared to the stepped surfaces, (012) and (102). Since this surface penetration reaction energy decreases the most for the most stable (001) facet, this surface/subsurface transition could be more sensitive to a tensile load than those studied here. Overall, we observe that atomic hydrogen prefers to bind at the stepped sites, but surface to subsurface diffusion could be more likely to occur from the (001) facet.

In addition to the thermodynamic properties, we have also computed activation barriers of hydrogen diffusion on the surface and the first subsurface via the nudged elastic band (NEB) method (Figure 4e). Here, the climbing image NEB (CI-NEB) method was employed to find the transition state and the minimum energy path (MEP) for each surface of interest. In this approach, a chain of 6–8 linear interpolation images along an initial pathway between the given initial and final states of a reaction is relaxed to determine the MEP and its corresponding saddle point. The images are relaxed along the energy pathway until the maximum residual forces on each atom are less than 0.01 eV/Å. The transition state was confirmed by the presence of one imaginary vibrational frequency.

The surface to subsurface MEPs and activation energies are calculated with a hydrostatic elastic tensile strain of up to 4%. Results are shown in Figure 5a for the α-U (001) surface (see Table S2 in the Supporting Information for the results of other facets). As hydrogen penetrates the (001) surface cell, it has to overcome an activation energy barrier of 0.82 eV on the surface with no strain, 0.69 eV with 1%, 0.63 eV with 2%, 0.57 eV with 3%, and 0.46 eV with 4% tensile load. These values are in close proximity to the experimental result of 0.502 eV for the activation barrier.6 This trend is similar to our results for the adsorption and absorption energies, as well as previous calculations of hydrogen diffusion in expanded bulk palladium supercells. In this case, stronger hydrogen bonding in the strained system likely also stabilizes the transition state, leading to lower activation energies overall. We also notice that the relative path from the adsorption site to the final subsurface absorption site gets shorter with tensile strain. This could be attributed to the reduction of the distance between the hydrogen adsorbate and the subsurface U atoms due to the decrease in interlayer spacing described in the above section. In addition, the plot of the activation barrier as a function of reaction energy (Figure 5b) shows a linear dependence while simultaneously showing an inverse relationship to the applied tensile load. Thus, this relationship can potentially be exploited as a predictive tool to estimate diffusional barriers for similar loads. As shown in Table S2, results for other surfaces follow a similar trend, with facets exhibiting lower adsorption energies (e.g., kinked vs terrace surfaces), showing higher activation diffusion barriers overall.

In order to further probe quantum nuclear vibrational effects, we have computed the ZPE for hydrogen surface adsorption and subsurface absorption, as well as those effects on reaction energies and transition states shown in Figure 4 (see Table S2 in the Supporting Information for detailed results). We observe that the ZPE occurs as a systematic correction for all surface and subsurface adsorption sites studied here. For example, surface adsorption results in a ZPE correction of 0.15 ± 0.02 eV, whereas subsurface absorption...
functional dependence, and the choice of a different functional could affect these results.\(^{59,60}\)

### 3.4. Coverage Dependence on Atomic Hydrogen Surface Adsorption and Subsurface Absorption

#### 3.4.1. ML Coverage Dependence

Adsorption on metal surfaces is governed by both the adsorbate–surface interactions and the adsorbate–adsorbate interactions that could be attractive or repulsive. Such interactions can significantly impact the kinetics and thermodynamics of processes on surfaces, such as ML formation, desorption, diffusion, phase transitions, and chemical reactions.\(^{61,62}\)

In the previous section, all of the adsorption calculations were performed on lower surface coverage, isolated systems (e.g., in the dilute limit). However, this dilute limit does not always correspond to experimental conditions, where a range of ML coverages can be explored. Here, we compute properties over a range of ML coverages, helping to bridge the gap between DFT and experiments.

In order to understand the effects of multiple hydrogen atoms, we assess the effect of increasing hydrogen coverage on adsorption unstrained surfaces. In this case, we calculate the energetic trend for an increasing ML coverage by computing the adsorption energy per H atom using the following formula

\[
E_{\text{ads}} = \frac{E_{(U/H)} - E_{(U)} - 1/2N_H E_{H_2}}{N_H}
\]

where \(E_{(U/H)}\) is the total energy of the system with adsorbates present, \(E_{(U)}\) is the total energy of the clean surface, \(E_{H_2}\) is the energy of the gas-phase hydrogen molecule, and \(N_H\) is the number of adsorbed hydrogen atoms. In our study, the full ML coverage corresponds only to the exothermic adsorption of hydrogen. For example, the (001) facet contains 20 possible adsorption sites (top, hollow, and bridge). However, only the first eight adsorbed hydrogens in hollow sites yielded exothermic adsorption. Therefore, for the (001) surface, we elaborate the adsorption behavior at coverages ranging from 1/8 ML to 1 ML.

In order to overcome the combinatorial issue associated with an exhaustive search for adsorbate–surface structures, we employ a greedy forward-stepwise sampling method.\(^{55}\) This approach allows for finding an adsorbate–surface configuration with a reasonably low energy using a minimal amount of computational resources. First, we determine the most favorable configuration for a single hydrogen atom on a given facet. Then, we take that configuration and add another hydrogen atom to different sites until we determine the lowest energy configuration for that particular coverage. The process is repeated stepwise until the full ML coverage is achieved.

As shown in Figure 6, different structural combinations at each specific ML coverage produce a dissimilar average adsorption energy. In addition, the average adsorption energy becomes more positive as more hydrogen adsorbs on any given surface. For the (001) surface (Figure 6a), the first H adatom prefers to bind to the hollow2 site, as previously described. At 0.25 ML coverage, the second hydrogen atom prefers to bind to the nearest hollow2 site. At this point, we observe some electrostatic screening from uranium atoms (flat line) as there are little to no interactions between two adsorbed hydrogen atoms that are spatially close to each other. In fact, the same preference occurs up until all hollow2 sites are occupied. At 0.5 ML coverage, the four hydrogen adatoms form a period zigzag structure on the α-U (001) surface. Newly added H atoms adsorb to nearby available hollow1 sites until all hollow sites are occupied at 1 ML coverage.

We observe similar trends on other terrace and stepped facets studied here (Figure 6b). At low coverage, we observe likely screening effects (flat line) in all surfaces, similar to those in the (001) case. In addition, the adsorption energy per hydrogen atom becomes more positive (repulsive) with increasing ML coverage. In terms of the energy scale, the kinked facets (012) and (102) start at lower energies (−0.71 and −0.66 eV/H, respectively) compared to terrace surfaces as they possess the most reactive stepped sites. As the coverage increases, the stepped sites on (012) and (102) fill up first, followed by adsorption at hollow sites in relatively (unkinked) flat regions of the surface. In contrast, in (010) and (100), we observe initial adsorption at hollow sites, followed by

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**Figure 6.** Adsorption energy per H atom on an α-U surface at different coverages: (a) (001) facet, (b) a cross-facet comparison including the (001) blue, (010) orange, (100) green, (012) red, and (102) purple α-U surfaces.
adsorption into bridge sites. For all surfaces, no exothermic adsorption occurs on top sites directly above U surface atoms.

3.4.2. Surface H/U Phase Diagram. All of our previous calculations were based on zero-temperature and zero-pressure optimizations. In order to connect our DFT calculations to actual thermodynamic measurements, we use the Python multiscale thermochemistry toolbox\(^3\) (pMuTT) to generate the surface phase diagram for equilibrium hydrogen adsorption. pMuTT is a Python library designed to estimate various thermochemical and kinetic properties from \textit{ab initio} data for heterogeneous catalysis. Here, the two-dimensional phase diagram is computed by finding the U/H surface configuration from our set of calculations that exhibits the lowest Gibbs free energy at a specific temperature and pressure. The Gibbs free energy for each adsorbate–solid structure is estimated in the harmonic limit, where each adsorbed hydrogen is treated as an independent quantum-harmonic oscillator, and its vibrational frequencies are computed via finite difference.

In Figure 7, each computed phase diagram shows the ML coverage as a function of pressure and temperature. Configurations with high ML coverage are more favored at high pressure and low temperature, whereas the clean \(\alpha\)-U surface is more prominent at low pressure and high temperature. As temperature increases, the entropy of the gas phase drives the desorption of hydrogen. Since hydrogen
adsorption on an \( \alpha \)-U surface is an exothermic reaction, the adsorption capacity increases with decreasing temperature. We also notice that only the (102) facet shows a complete ML coverage at low temperatures (\( \sim 150 \) K) and high pressure (\( >1 \) bar) over the range of conditions studied here. On the other hand, facets behave differently at various nonextreme cases. If we look at ambient conditions of 300 K and a realistic partial pressure of hydrogen gas in air (\( \sim 10^{-4} \) bar), these stepped surfaces have higher ML coverages than the terrace facets. Specifically, the (012) and (102) facets have 0.56 ML coverage at these conditions, while (001), (100), and (010) have smaller ML coverages of 0.38 ML, 0.5 ML, and 0.25 ML, respectively. At 600 K, which is the operating temperature of some nuclear reactors, and at \( \sim 10^{-5} \) bar hydrogen partial pressure, we notice a similar trend. We note that this temperature is above the transition point for \( \alpha \) to \( \beta \)-UH\(_3\) under atmospheric pressure. The stepped facets have a ML coverage of 0.17 ML, while the terrace surfaces have 0 ML coverage. Overall, we observe that the ML coverage is generally more significant for stepped surfaces over all conditions studied here, consistent with the conventional notion that these surfaces are likely much more reactive than their terrace counterparts.

### 3.4.3. Subsurface Adsorption as a Function of Surface Coverage

We now investigate the possibility of surface adsorption either mitigating or enhancing subsurface adsorption for a nontensile loaded system. Our goals are to potentially find a cross-over point where hydrogen subsurface adsorption becomes more favorable compared to surface adsorption for various facets of interest. We compute the energy to add hydrogen into either the first subsurface layer or on the surface itself for each ML coverage using the following equation

\[
E_{\text{addsurf} / \text{addsubsurf}} = E_{\text{(U/NH+1)}} - E_{\text{(U/NH)}} - \frac{1}{2}E_{\text{H}_2}
\]

Here, \( E_{\text{(U/NH+1)}} \) is the energy of the system with \( N + 1 \) surface adsorbates (for \( E_{\text{add surf}} \)) or the energy of the system with \( N \) surface adsorbates and one subsurface hydrogen (for \( E_{\text{add subsurf}} \)). \( E_{\text{(U/NH)}} \) is the total energy of the system with \( N \) surface adsorbates, and \( N \) is the number of adsorbed hydrogen atoms.

Table 6 shows the results for the surface coverage of the (001) facet. At zero ML, adding an H atom to the surface is favored over the subsurface; in fact, subsurface adsorption is endothermic (+0.16 eV), while surface binding is exothermic (−0.57 eV). The most stable subsurface site at this point is used in subsequent calculations at higher coverages. Subsurface adsorption becomes exothermic at 1/8 ML coverage, though adding hydrogen to the surface is still more favored. This trend continues until 3/8 ML coverage, where the subsurface absorption (−0.36 eV) becomes preferred over surface absorption (−0.26 eV). Further details on the other low index terrace and kinked surfaces and the results are presented in Supporting Information, Table S3. For all other facets studied here, subsurface absorption was either endothermic or still less favorable compared to the surface adsorption. As a result, (001) is the most likely candidate from our specific set that appears able to initiate subsurface hydriding at higher ML coverage.

### 4. CONCLUSIONS

In this work, we have investigated uranium hydriding from two perspectives: (1) as a function of applied tensile load on an \( \alpha \)-U lattice and (2) formation of hydrogen ML coverage. First, we have analyzed the adsorption, absorption, and diffusion of hydrogen from the surface to the first subsurface layer under the applied symmetric tensile strain of up to 4%. Absorption sites closest to the surface were found to be the most favorable and exhibited either tetrahedral or square-pyramidal geometries. Both surface and subsurface binding energies were found to be sensitive to the hydrostatic elastic tensile strain, leading to lower values overall. In fact, a tensile strain of only 2% is required for subsurface absorption to become an exothermic process, though this value could shift somewhat depending on the choice of the DFT functional and inclusion of ZPE effects. In addition, the energy difference between surface adsorption and first-layer subsurface absorption becomes less positive with increasing tensile strain. These tensile strain states are likely thermally accessible under ambient conditions. Similar to the binding energies, the diffusion barriers were found to be responsive to strain and exhibited an inverse linear relationship as a function of reaction energy, yielding a new predictive capability for this process.

We also explore the hydriding process from the perspective of the formation of a hydrogen ML on the uranium surface. Coverage studies for all facets showed that the adsorption energy becomes more positive as more hydrogen atoms adsorb on the surface. We observe that the kinked (012) and (102) facets initially exhibit higher exothermic adsorption energies compared to those of the terrace surfaces. As shown in our phase diagrams, they also show larger ML coverages with increasing pressure and temperature. Also, calculation of the energetic cost of inserting additional hydrogen inside the first subsurface layer of the (001) facet showed the following: (1) at 1/8 ML, subsurface absorption becomes exothermic, and (2) at 3/8 ML, this absorption is energetically favored over surface adsorption. This trend was only observed for the (001) facet in our study. Hence, we have found that high ML coverage is more likely on the (102) surface, with 56% coverage possible under ambient conditions. In contrast, (001) ML formation is more likely to enhance subsurface penetration. Hydrogen diffusion kinetics from a metallic surface to its subsurface is strongly affected by the ML coverage, which is the subject of future investigations. The types of results presented in our work can be important inputs for larger-scale models, such as kinetic Monte Carlo, that can further bridge the time and length scale gap with experiments. This could include looking at defect systems, larger-scale models that can bridge gaps with experiments, and varied atmospheric conditions.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.2c01170.

Graphics of α-U (012) and (102) kinked surfaces, sample minimum energy pathway plots as a function of tensile load, interlayer and U–U bond distance comparison as a function of tensile strain for common terrace surfaces, comparison of surface versus subsurface adsorption energies as a function of tensile strain, and computed adsorption energies to add an additional hydrogen atom on the α-U surface or in the first subsurface layer as a function of coverage (PDF)

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Notes
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