Investigation of adsorption, dissociation, and diffusion properties of hydrogen on the V (1 0 0) surface and in the bulk: A first-principles calculation

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Highlights

- Interaction between H and V surface and bulk are fully studied.
- H coverage \((\theta)\) effects the adsorption energy of \(\text{H}_2/\text{V}(1\ 0\ 0)\).
- H solubility and diffusivity depend slightly on the H concentration.

Graphical Abstract

Schematic of H permeation of dense metallic membrane.

Abstract

To investigate the H\(_2\) purification mechanism of V membranes, we studied the adsorption, dissociation, and diffusion properties of H in V, an attractive candidate for H\(_2\) separation materials. Our results revealed that the most stable site on the V (1 0 0) surface is the hollow site (HS) for both adsorbed H atoms and molecules. As the coverage range increases, the adsorption energy of \(\text{H}_2\) molecules first decreases and then increases, while that of H atoms remains unchanged. The preferred diffusion path of atoms on the surface, surface to first subsurface, and first subsurface to second subsurface is HS ? bridge site (BS) ? HS, BS ? BS, and BS ? tetrahedral interstitial site (TIS) ? BS, respectively. In the V bulk, H atoms occupy the energetically favourable TIS, and diffuse along the TIS ? TIS path, which has
Introduction

Energy resource exhaustion is among the most important challenges facing humankind, and the development of new energy sources has become urgent worldwide. H₂, a safe, green, and environmentally friendly renewable energy source, is considered one of the best alternatives to fossil fuels in the future [1,2]. The production, purification, and storage of H₂ have always attracted considerable research attention. Separation and purification techniques of H₂ determine the application standards of H₂ fuel [2–4]. To meet the industrial demand for high-purity H₂, H₂ purification is necessary. Currently, industrial methods for H₂ recovery mainly include membrane separation, pressure-swing adsorption, and cryogenic separation [4,5]. Membrane separation is considered the most promising third-generation gas separation technology, after pressure-swing adsorption and cryogenic separation, because it is economical, convenient, efficient, and clean. Moreover, H₂-selective metallic membranes have received much attention for purification. Although Pd-based metallic membranes are the most mature and widely used materials in current research, they are disadvantageous for large-scale production because they are high in cost [6]. Consequently, many researchers have searched for alternatives to reduce costs. Group VB metals (V, Nb, and Ta) have received significant attention because they show better hydrogen permeability, higher mechanical strengths, and lower costs than Pd-based metals [7,8]. V, which has the highest H diffusion coefficient among group VB metals, is currently considered promising as a H₂ separation material [5,9]. In addition, V and its alloys are not only considered important H₂ storage materials with a large H capacity [8], but also candidate materials for the first walls and blankets of fusion reactors because of their excellent low activation characteristics under neutron irradiation, remarkable high-temperature performance, and swelling resistance under neutron radiation [10]. Until now, many researchers have performed many experiments and theoretical studies on V-based permeable membrane materials, mainly concentrating on the bulk [10–16]. For instance, a work by Dolan et al. showed that a Pd catalyst layer-coated 0.25 mm V substrate exhibited a high permeability under H₂ permeation processes have been investigated in detail for metallic membranes. In this study, we systematically studied the adsorption and diffusion properties of H atoms on the V surface by using first-principles methods. Specifically, all possible stable positions, diffusion energy barriers, and electronic properties of H atoms adsorbed on the V (1 0 0) surface were calculated [23–27], as well as the solution energy and diffusion energy barrier of H in bulk V. We also considered the calculation of adsorption structures from low coverage to high coverage. This work is of great significance for a comprehensive understanding of the mechanism by which H atoms interact with metal surfaces; it provides a theoretical basis for further research on V-based alloys for H₂ storage and H₂ separation and purification applications.

Materials and methods

All calculations were performed using the Vienna Ab initio Simulation Package code [28,29]. Perdew–Burke–Ernzerhof generalised gradient approximation functions [30] and the projected augmented wave method [31,32] were used to treat the core–electron interactions. V is a VB group transition metal element, and its valence electron structure with H is 3d³4s² and 1 s¹, respectively. The kinetic cut-off energy of 360 eV was applied to all systems. The Brillouin zone was sampled by a grid of k-points with the resolution 2π × 0.03 Å⁻¹. During geometric optimisation, the energy difference tolerance was less than 1 × 10⁻⁶ eV atom⁻¹ and the force interacting on each atom was less than 1 × 10⁻² eV Å⁻¹. To search the minimum diffusion paths and transition states of the H atom, we employed the climbing image nudged-elastic-band (CI-NEB) method to calculate the H diffusion energy barriers between the optimised initial and final sites [33].

To optimise the computational cost and the accuracy of the DFT calculations, we built a seven-layer slab of the (2 × 2) V (1 0 0) surface with a vacuum region of 15 Å. Atoms in the upper three V layers were allowed to relax, while those in the bottom four layers were fixed at their bulk positions. The H atoms were placed at the top site (TS), bridge site (BS), and hollow site (HS) in the V surface. The TIS, OIS, and diagonal interstitial site (DIS) were considered for the diffusion of H atoms in the subsurface and bulk, for which 2 × 2 × 2, 3 × 3 × 3, and 4 × 4 × 4 supercell models containing 16, 54, and 128 V atoms, respectively, were built.

The change in the interlayer distance between the slab and bulk model is given by [27]

\[ \Delta d = \frac{d_{i,j} - d_0}{d_0} \]  

where \( d_0 \) and \( d_{i,j} \) are the interlayer distances between the \( i \)th and \( j \)th layers of the slab model before and after relaxation, respectively. Positive \( \Delta d \) indicates expansion between the layers, while negative \( \Delta d \) indicates contraction.

The surface energy \( \gamma_s \) is an important parameter for describing the basic properties of a metal surface, including the surface stability as well as physical and chemical reactions. A lower surface energy indicates better structural stability. It is defined as [34]
where $E_{\text{relax}}$, $E_{\text{unrelax}}$, $E_{b}$, $A$, and $N$ represent the total energy of the pre-relaxation model, total energy of the model after relaxation, bulk energy per atom, surface area of the cut surface structure, and number of atoms in the slab, respectively.

The average adsorption energy ($E_{\text{ads}}$) of H atoms is expressed as:

$$E_{\text{ads}} = \frac{1}{N} (E_{\text{slab}} - HE_{\text{H}} - NHE_{b})$$

(3)

Here, $E_{\text{slab}}$, $E_{\text{H}}$, and $E_{\text{slab+H}}$ are the total energies of the H$_2$-adsorbed system, $E_{\text{slab}}$ is the total energy of the slab, $N$ is the number of H$_2$ molecules or H atoms adsorbed, and $E_{b}$, $E_{\text{H}}$, and $E_{\text{slab}}$ are the total energies of free H$_2$ molecules and H atoms, respectively. Lower H molecular or atomic adsorption energies correspond to more stable adsorption positions.

The solution energy ($E_{\text{sol}}$) of the interstitial H atom in bulk bcc V can be obtained as:

$$E_{\text{sol}} = E_{b} + E_{\text{H2}} - \frac{1}{2} E_{\text{H2}}$$

(5)

where $E_{\text{sol}}$ and $E_{\text{H2}}$ are the total energies of the supercell with one H atom and no H atom, respectively. $N$ represents the number of V atoms and $E_{b}$ is the total energy of one H$_2$ molecule.

**Results and discussions**

**Surface model**

To obtain a reliable and stable surface, we selected the V (1 0 0) surface of four to nine atomic layers for geometric relaxation. The calculated changes in the interlayer relaxation and surface energies are listed in Table 1. It is seen that the change in the relaxation of the distance between the first and second atomic layer ($\delta d_{1-2}$) values is greater, while the other layer distance changes are slightly weaker. The $\delta d_{1-2}$ values are negative, indicating that the surface atomic layers are contracted, while the $\delta d_{3-4}$ values excluding the five-slab model are positive, showing that the surface atomic layers are expanded. In addition to the surface energy of the seven-slab model agreeing with the experimental result, we observe that the surface energy of the other slab model tends to stabilise at 0.150 eV/Å$^2$ as the thickness of the slab increases in general; this is consistent with the calculated values [37]. Therefore, the seven-slab model can be utilised for further study.

**Adsortion energy**

To determine the stability of H atom adsorption sites in the V (1 0 0) surface, we investigated the possible adsorption sites of a single H atom, as shown in Fig. 1(a-k). For the bcc metal (1 0 0) surface, H is mainly adsorbed at surface sites including the TS, BS, and HS. Additionally, H is mainly adsorbed at the first and second subsurface sites, such as the TIS, OIS, and DIS. The calculated adsorption energies of the H atoms at these sites are presented in Table 2. It can be seen that the HS has a stronger adsorption energy of $-2.945$ eV among all TSS, BSs, and HSs under a molecular layer (ML) surface coverage of 0.25; their vertical distances from the surface are 1.723, 1.228, and 0.564 Å, respectively, which implies that H prefers to adsorb at the HS. For the subsurface adsorption sites, we can see in Table 2 that TIS (1) has a minimum adsorption energy of $-2.407$ eV; those of TIS (2) and DIS (1) are respectively $-2.275$ eV and $-2.214$ eV; and that of OIS (1) is $-2.065$ eV; therefore, H is preferentially adsorbed at TIS (1). Similarly, TIS (3) shows a minimum adsorption energy in the second subsurface, which indicates that H-binding sites are energetically stable. In the analysis above, H atoms are most strongly attached to the surface compared to the first and second substrates. In addition, our calculated values show consistency with those reported in the literature [38].

### Table 1

| Slab model | $V$ (1 0 0) | $\delta d_{1-2}$ (%) | $\delta d_{2-3}$ (%) | $\delta d_{3-4}$ (%) | $\gamma_s$ (eV/Å$^2$) | $\gamma_s$ (J/m$^2$) |
|------------|-------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 5 layers   | -15.83      | 2.08                 | -0.48                | 0.150                | 2.39                 |
| 6 layers   | -14.46      | -0.34                | 2.57                 | 0.150                | 2.39                 |
| 7 layers   | -13.82      | -0.02                | 2.72                 | 0.152                | 2.44                 |
| 8 layers   | -15.39      | 0.19                 | 2.29                 | 0.150                | 2.39                 |
| 9 layers   | -15.56      | -0.10                | 2.31                 | 0.150                | 2.39                 |
| Cal. [37]  | -12.41      | 0.24                 | 2.87                 | 0.150                | 2.40                 |
| Exp. [37]  | -6.67       | 0.99                 | 2.55                 |                      |                      |

To determine the structural properties of bcc V, the equilibrium lattice constant was 2.996 Å for bcc V, which agrees with other theoretical (2.998 Å) [35] and experimental (3.03 Å) [36] values. Moreover, the calculated elastic constants ($C_{11} = 262.9$, $C_{12} = 136.7$, and $C_{44} = 38.7$ GPa) and elastic moduli ($B = 178.8$, $E = 130.0$, and $G = 47.1$ GPa) also agree with both experimental and theoretical results.

\[
\gamma_s = \frac{1}{2A} (E_{\text{relax}} - NE_b) - \frac{1}{A} (E_{\text{relax}} + E_{\text{unrelax}})
\]

(2)

where $E_{\text{relax}}$, $E_{\text{unrelax}}$, $E_{b}$, $A$, and $N$ represent the total energy of the pre-relaxation model, total energy of the model after relaxation, bulk energy per atom, surface area of the cut surface structure, and number of atoms in the slab, respectively.
We further studied the interaction between H2 and the V (1 0 0) surface, where the initial configuration of H2 was first divided into vertical versus parallel to the V (1 0 0) surface. Fig. 1(l–n) shows the adsorption model of the HS, which is labelled as a, b, and c states in our study. Based on the previous calculation results, the vertical distance of a single H atom adsorbed on the surface of V (1 0 0) is about 0.564–1.725 Å, so the distance between the centre of the H2 molecule at the initial position and the surface (dH2-surf) is set as 1.725 Å. The calculation results we obtained are presented in Table 3. The H–H bond length (dH–H) is ~0.751–0.753 Å, almost equal to our calculation for that of free H2 (0.75 Å), indicating that H2 is not dissociated and is adsorbed to the surface in molecular form. This is because the V atoms on the surface are very far away from H2 at this initial distance with only a weak interaction that does not break the H–H bond. The vertical height between the H2 molecule and V surface is ~3.468–4.370 Å. Compared to the b and c states, molecular H2 is preferentially adsorbed at the TS, BS, and HS in the a state with corresponding adsorption energies of ~0.001, ~0.003, and ~0.005 eV, respectively. This demonstrates that the interaction between H2 and the V surface is exothermic and that the adsorption energy of the HS is much smaller than those of the other sites, further indicating that H2 is more inclined to adsorb on the HS of the (1 0 0) surface. However, the TS shows the same adsorption energy of ~0.001 eV for a molecule oriented in a parallel or perpendicular manner.

**Electronic properties**

To investigate the electronic properties of H atom absorption at the TS, BS, and HS, we calculated the total density of states (TDOS) and the project density of states, as well as the charge density difference, as depicted in Fig. 2. Fig. 2(a) shows that the peak position of the TDOS and the splitting of the peak are significantly different after the adsorption of H atoms, and that the TDOS of H adsorption at different sites clearly varies. Significant hybridisation occurs between the H s and V d states, and the V s/p/d states overlap with the H s state below the Fermi level. In comparison to the TS and BS, the TS has a clear peak at ~6 to ~7.5 eV, indicating a strong chemical interaction between H and V atoms. Furthermore, we calculated the Z-direction planar-averaged charge density differences,
as indicated in Fig. 2(b). The cyan and yellow regions mark areas of charge depletion and accumulation, respectively [39]. Charge redistribution largely occurs between the nearest-neighbour layer V atoms and the H atom interface region; at the bottom layer of the V atom, farther from the H atom, almost no charge change is observed. A positive value indicates electron accumulation, while a negative value indicates electron depletion [40]. Accordingly, the electrons are transferred from the V (1 0 0) surface side to the H-atom side. To quantify the change in charge density, we also employed Bader charge analysis, which showed that the H atoms at the TS, BS, and HS have 0.4757, 0.5507, and 0.5965 e, respectively. As far as we know, more negatively charged H atoms have lower energies [20]. This is why the H atom is adsorbed more stably at the TS than at the other sites.

### Dissociation of H₂ molecules

In order to study the dissociation of H₂ molecules on the V (1 0 0) surface, the above calculation results indicate that the vertical adsorption of H₂ molecules is more stable than parallel adsorption; therefore we calculate the dissociation of the H₂ molecule from the initial adsorption at the HS on the surface, as depicted in Fig. 3. As shown, the H₂ molecule does not dissociate at the beginning of the HS. With gradual decreases in the vertical distance (d₃₃-surf) between the H₂ molecule and surface, the H–H bond begins to break. At a distance of 0.761 Å from the surface, significant H bond fracture occurs, indicating that H₂ dissociation depends on the initial distance of H₂ from the surface. The bond length, dissociation energy, and vibration frequency of a single H₂ molecule were calculated as 0.752 Å, 4.511 eV, and 4262 cm⁻¹, respectively, differing only slightly from both theoretical (respectively 0.751 Å, 4.51 eV, and 4266 cm⁻¹) and experimental (respectively 0.741 Å, 4.75 eV, and 4301 cm⁻¹) values [25,41]. Combining the adsorption energy of the H atom and H₂ molecule calculated above, the undissociated H₂ molecule is weakly physically adsorbed to the (1 0 0) surface, while the dissociated H atom is strongly chemically adsorbed. The physical adsorption energy of H₂ is much larger than the chemical adsorption energy of H on the (1 0 0) surface, and the relaxed and stable position is significantly different from the surface height.

### Diffusion of H atoms

We studied the diffusion properties of H atoms on the V surface. H₂ molecules at the surface of V (1 0 0) dissociate into H atoms that may diffuse either on the surface or from the surface to the subsurface, and then gradually into the interior. Using the CI-NEB method, the calculated H diffusion barrier energy is presented in Fig. 4. The number given in the figure indicates possible H diffusion paths. We first analyse Fig. 4(a), showing surface diffusion, and observe that the H diffusion barrier energy is 0.251 eV from the HS to BS, with further diffusion to the HS having a barrier energy of 0.132 eV. Thus, the total H diffusion barrier energy along the HS → BS → HS path is 0.383 eV. In addition, the H atom diffusing along the HS → TS → HS path has a diffusion barrier energy of 0.785 eV. These results indicate that the H atom preferentially difuses along the HS → BS → HS path. Fig. 4(b) illustrates H diffusion from the surface to the first subsurface. Diffusion along the HS to TIS (1) requires an energy of 0.574 eV, while the diffusion barrier energy between the BS and TIS (1) is slightly smaller at 0.547 eV, indicating that the former path is unfavourable. We also analyse the case of diffusion from the first to second subsurface in Fig. 4(c). The diffusion barrier energies for TIS (1) → TIS (3) through OIS (1) and TIS (1) → TIS (2) → TIS (3) are comparable at 0.464 and 0.348 eV, respectively, making the latter process energetically favourable. In conclusion, the optimal diffusion pathway for H atoms is 3 → 6 → 7 from the surface to the first subsurface to the second subsurface. This indicates that the decisive step of H atoms diffusing from the surface to subsurface is the passage through the surface of the first atomic layer. Once the H atom is below the surface, downward diffusion occurs easily. Moreover, deep diffusion of the H atom is likely to approaching the diffusion energy barrier of the bulk.

### Table 2
Calculation results for H adsorbed on V (1 0 0) surfaces at 0.25 ML: adsorption energy (E_ads), short distance between H atom and V atom (d₁₋₃), and adsorbate height (d₃₋₄surf).

| Site       | E_ads (eV) | d₁₋₃ (Å) | d₃₋₄surf (Å) |
|------------|------------|-----------|---------------|
| Surface    |            |           |               |
| TS         | −2.150     | 1.725     | 1.725         |
| BS         | −2.826     | 1.834     | 1.228         |
| HS         | −2.945 (−2.97) [38] | 1.846     | 0.564         |
| First subsurface |            |           |               |
| TIS (1)    | −2.407 (−2.43) [38] | 1.761     |               |
| TIS (2)    | −2.275     | 1.706     |               |
| OIS (1)    | −2.065     | 1.634     |               |
| DIS (1)    | −2.214     | 1.671     |               |
| Second subsurface |        |           |               |
| TIS (3)    | −2.399 (−2.29) [38] | 1.723     |               |
| TIS (4)    | −2.477     | 1.728     |               |
| OIS (2)    | −2.275     | 1.658     |               |
| DIS (2)    | −2.347     | 1.674     |               |

### Table 3
Calculation results of H₂ adsorbed on V (1 0 0) surfaces at 0.25 ML.

| Site       | E_ads (eV) | d₁₋₃ (Å) | d₃₋₄surf (Å) |
|------------|------------|-----------|---------------|
| a state    |            |           |               |
| TS         | −0.001     | 0.753     | 3.478         |
| BS         | −0.003     | 0.753     | 3.473         |
| HS         | −0.005     | 0.753     | 3.476         |
| b state    |            |           |               |
| TS         | −0.001     | 0.753     | 3.475         |
| BS         | 0.006      | 0.752     | 3.475         |
| HS         | 0.004      | 0.751     | 4.370         |
| c state    |            |           |               |
| TS         | −0.001     | 0.753     | 3.468         |
| BS         | 0.006      | 0.753     | 3.475         |
| HS         | 0.008      | 0.751     | 3.908         |
Surface coverage

We studied the effects of different surface coverage on the H adsorption energy. H coverage ($\theta$) is defined as the ratio of the number of adsorbed H atoms (or molecules) to the number of metal atoms in each layer of the surface, considering the different permutations of H adsorption configurations. Previous calculations indicate that H$_2$ molecules are more stable when adsorbed vertically on the surface, so only the adsorption energy of vertical H$_2$ molecules on the surface is calculated here. We calculated many average adsorption energies of H atoms and molecules at different sites with changes in $0.25 < \theta < 1$, and found that, under the same coverage of H atoms or molecules, the adsorption energy calculated at the same adsorption sites or equivalent sites is not significantly different and that H atoms or molecules are more stable at the HS. To understand the relationship between the H atoms or molecules and coverage, the minimum adsorption energy of stable configuration is given as a function of coverage, as plotted in Fig. 5 (a, b). The adsorption energies of H atoms at the TS and BS gradually increase with increasing coverage from 0.25 to 1 ML, as indicated in Fig. 5(a). This may be attributed to electrostatic repulsion between atoms and an increased electrostatic energy, indicating the existence of repulsion between the adsorbed H atoms. The adsorption energy of H atoms adsorbed at the HS is unchanged with varying coverage, indicating that the interaction between the adsorbed H atoms is weak. Subsequently, we analyse the adsorption of H$_2$ molecules. Fig. 5(b) shows that the adsorption energy of H$_2$ decreases in the range of 0.25–0.5 ML and increases in the range of 0.5–1 ML, indicating that $\theta < 0.50$ ML facilitates adsorption at all three sites. For $\theta > 0.50$ ML, that is, as the number of adsorbed H$_2$ molecules increases, the stability of H molecular adsorption decreases.

H dissolution and diffusion in bulk V

The last issue we considered was the solubility and diffusion properties of H atoms in the bulk. When metal reacts with H to form gap-type hydrides, H generally occupies the TIS, DIS, and OIS in metal lattices. The calculated solution energy ($E_{sol}$) of H atoms in the TIS, DIS, and OIS is $-0.346$, $-0.238$, and $-0.165$ eV for $V_{16}H$, $-0.371$, $-0.336$, and $-0.228$ eV for $V_{54}H$, and $-0.41$, $-0.336$, and $-0.284$ eV for $V_{128}H$, respectively. Our calculations

![Fig. 2](image-url)
are well matched to the reference values \[5,14,21,22\]. The \(E_{\text{sol}}\) value of the TIS is much lower than those of the DIS and OIS within the entire H concentration range, implying that the most stable configuration is the TIS. Fig. 5(c) shows \(E_{\text{sol}}\) of the V–H system depending slightly on the H concentration. The \(E_{\text{sol}}\) values of the TIS, DIS, and OIS generally increase with H concentration, indicating that the V–H system is energetically unfavourable. We then analysed H solubility, which is critical in determining the recombination rate coefficient and is directly related to the capture and bubbling of H, as illustrated in Fig. 5(d). The concentration of H decreases as the temperature increases, indicating that the dissolution of H in V is exothermic. Moreover, H has a high concentration at room temperature, directly leading to the accumulation of H atoms at defects followed by precipitation to form H\(_2\), causing the phenomenon of hydrogen embrittlement in the metal. Suzuki et al. reported that a sharp ductile-to-brittle transition occurred at \(-0.2–0.25 \text{ H/M for V membranes}\) \[15\].

H diffusion follows two different paths among neighbour TISs, as shown in Fig. 6. On the first path, H atoms diffuse through a DIS (see Fig. 6(a)), while on the second path, they diffuse through an OIS (Fig. 6(b)). The preferred H diffusion pathway is the first path, which is more energetically favourable than the second path. The diffusion barrier first decreases and then increases with H concentration. In addition, both the DIS and OIS are second-order
saddle points on the potential energy surface. Sorescu et al. also proved such a case occurring in bcc bulk Fe [26]. Consequently, H diffusion mainly occurs between adjacent TISs. We further discussed the diffusion coefficient of H, which measures the ability of H atoms to diffuse across a metallic membrane. To match the experimental components and enable comparison [4, 7], we chose to study the diffusion coefficient of H in the V16H phase using the Arrhenius diffusion equation [42,43], as illustrated in Fig. 6 (c). At an operating temperature of 673 K, the value is $1.73 \times 10^{-8}$ m$^2$ s$^{-1}$, unlike the existing experimental and calculated values of $1.2 \times 10^{-8}$ [7] and $1.25 \times 10^{-8}$ m$^2$ s$^{-1}$ [4], respectively. This may arise from differences in calculations and experiments, especially in the activation barrier of H. In addition, the diffusivity increases with temperature.

Conclusion

In summary, we have employed a combination of first-principles methods and empirical theory to study the adsorption, dissociation, and diffusion properties of H on the V (1 0 0) surface and in the bulk. Our calculation results indicate that the most stable adsorption configuration with different coverages of H atoms and molecules on the surface is the HS. Specifically, the HS is the most thermodynamically stable site for H atom adsorption, with an almost constant adsorption energy at 0.25–1 ML coverage. H$_2$ molecules tend to become adsorbed vertically at the HS on the surface, showing a very weak physical adsorption state. With increasing coverage, the adsorption energy first decreases and then decreases. In addition, H$_2$ molecules gradually dissociate into H atoms as they approach the surface. The diffusion of H atoms on the surface, from the surface to the first subsurface, and from the first subsurface to the second subsurface, optimally occurs via the paths of HS → BS → HS, BS → BS, and BS → TIS → BS, respectively. For the bulk, we find that H atoms occupy the most stable TIS and diffuse along adjacent TISs. At the operating temperature of 673 K, the H diffusion coefficient is $1.73 \times 10^{-8}$ m$^2$ s$^{-1}$ for V$_{16}$H. This study is important for the next step of alloying element doping, regulation, and Pd plating to obtain better H permeability in membrane metals.

Compliance with ethics requirements

This article does not contain any studies with human or animal subjects.

Declaration of Competing Interest

The authors declare that they have no conflicts of interest.

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Fig. 6. Calculated (a) TIS → DIS → TIS and (b) TIS → OIS → TIS of diffusion barrier energy of H in pure V as a function of H concentration, as well as (c) diffusion coefficient of H in pure V as a function of reciprocal temperature.
