



Enhanced hydrogen diffusion in magnesium based hydride induced by strain and doping from first principle study



J. Zhang^{a,*}, H. Qu^a, S. Yan^a, G. Wu^{a,**}, X.F. Yu^a, P. Peng^b

^a Key Laboratory of Lightweight and Reliability Technology for Engineering Vehicle, The Education Department of Hunan Province, Changsha University of Science and Technology, Changsha, 410114, China

^b College of Materials Science and Engineering, Hunan University, Changsha, 410082, China

ARTICLE INFO

Article history:

Received 22 August 2016
Received in revised form
21 September 2016
Accepted 7 October 2016
Available online 8 October 2016

Keywords:

Magnesium based hydride
Dehydrogenation kinetics
Strain
Transition metals
Diffusion energy barrier
First-principles calculations

ABSTRACT

Magnesium based hydride (MgH_2) is a promising hydrogen storage material. However, the sluggish sorption rate impedes its practical applications. To improve the dehydrogenation kinetics of MgH_2 , the influences of external strains with different dimension (uniaxial/biaxial/triaxial), direction (tensile/compressive) and magnitude ($-3\% \sim +3\%$) on H atom diffusion properties within MgH_2 lattice are investigated for the first time using first-principles calculations method. In addition, the synergistic effects of strain and doping of transition metal Nb are further studied. The results show that the diffusion energy barrier of H atom is sensitive to the strain applied to MgH_2 lattice. The energy barrier value decreases significantly upon no matter uniaxial, biaxial or triaxial strain, leading to the remarkable increase of H atom diffusion rate. By contrast, the uniaxial tensile strains of $\epsilon \geq 0.5\%$ along [100] or [010] crystal direction, biaxial and triaxial compressive strains of $\epsilon \leq -2\%$ are more beneficial to improving the dehydrogenation kinetics of MgH_2 . What's more, the strain and Nb doping play the synergistic enhancement effect in increasing H atom diffusion rate, which is superior to their separate role. Analysis of electronic structures reveals that the dehydrogenation kinetics of different MgH_2 systems is associated with the energy gap value near Fermi level and the covalent bond strength between hydrogen and metal ions within MgH_2 lattice. These results prompt a new insight to enhance the dehydrogenation kinetics of MgH_2 by synergistically introducing external strain and transition metal catalysts.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Increasing energy and environmental issues have stimulated the search for alternative and sustainable clean energy. Hydrogen is an ideal energy carrier because of its abundance and environmental friendliness. The safe and efficient hydrogen storage is the key to the success of hydrogen economy [1]. Magnesium based hydride (MgH_2) have received great attention for its high hydrogen volumetric-gravimetric capacity ($7.6 \text{ wt}\%/110 \text{ kg/m}^3$), light weight and low cost. However, the sluggish sorption kinetics and high dehydrogenation temperature ($\sim 300 \text{ }^\circ\text{C}$) limit its practical applications [2]. Numerous attempts have been performed to settle these problems over the past few decades. Some methods such as nanostructuring, catalyzing and forming composites exhibit

excellent effects in improving the dehydrogenation and rehydrogenation properties of MgH_2 [3–5].

As far as the hydrogen sorption kinetics of is concerned, nanostructuring is conducive to shortening H atom diffusion distance in Mg/ MgH_2 matrix. The added catalysts can prompt H_2 molecule dissociation or recombination on Mg/ MgH_2 surface. The abundant interfaces in composites can provide more diffusion paths for H atom. These benefits all contribute to the enhancement of sorption kinetics of Mg–H system.

Recently, the external strain (stress) has been proved to play an essential role in tuning the performance of hydrogen storage materials, especially for the low dimensional nanomaterials. For example, Zhou et al. [6] reported that the applied strain to graphene not only stabilizes the supported metal atoms and prevents them from clustering, but further increases the hydrogen storage capacity. Pivak et al. [7] reported that the compressive stress strongly changes the formation and decomposition enthalpy of Pd–H films and alters their thermodynamic properties. As for Mg–H system, it has also reported that its thermodynamics is sensitive to applied

* Corresponding author.

** Corresponding author.

E-mail addresses: zj4343@126.com (J. Zhang), wug1999@163.com (G. Wu).

external strain (stress). For example, Baldi et al. [8] found that the stress induced by interfacial elastic clamping in Ti/Mg/X/Pd (X = Pd, Ni) multilayers tunes the thermodynamics of Mg layer and increases hugely its hydrogen equilibrium pressure. Ham et al. [9] demonstrated that stress-induced orthorhombic Mg hydride (O–MgH₂) is thermodynamically destabilized at 373 K or lower. They found that the drastic destabilization arises from large tensile stress in single layer O–MgH₂ bonded to rigid substrate, or compressive stress due to large volume change incompatibility in Mg/Nb multilayers. Our recent studies also showed that the applied external strain decreases substantially the hydrogen desorption enthalpy of MgH₂. Particularly, the triaxial tensile strain is found to be more conducive to improving the dehydrogenation thermodynamics of MgH₂ [10]. However, few studies associated with strain effects on hydrogen sorption kinetics of Mg–H system have been reported to date, and whether the strain can tune the kinetics of MgH₂ is still unknown. To address these issues, the strain effects with different dimension (uniaxial/biaxial/triaxial), direction (tensile/compressive) and magnitude (–3% ~ +3%) on dehydrogenation kinetics of MgH₂ are systematically investigated for the first time using first-principles calculations method in this work. Based on the excellent catalytic role of transition metals in improving sorption kinetics of Mg–H system [11], the synergistic effects of strain and doping of transition metal on dehydrogenation kinetics of MgH₂ are further studied. The obtained results are expected to provide an insight for developing high performance Mg/MgH₂-based hydrogen storage materials by synergistically introducing external strain and transition metal catalysts.

2. Computational details

The first-principles calculations are performed using the CASTEP package [12] in this work. The ultrasoft pseudopotential [13] and generalized gradient approximation (GGA) in Perdew–Burke–Ernzerhof (PBE) format [14] are chosen for the electron–ion and electron–electron interactions, respectively. The plane wave cutoff energy of 310 eV and a $4 \times 4 \times 7$ k-points mesh in Brillouin zone [15] are employed for all MgH₂ models. The convergence criteria for energy, force, stress and displacement are 2.0×10^{-5} eV/atom, 0.05 eV/Å, 0.1 GPa and 0.002 Å, respectively.

MgH₂ exhibits the tetragonal rutile structure with space group $P4_2/mnm$ at ambient conditions [10]. Its lattice constants are $a = 4.501$ Å and $c = 3.010$ Å. Each Mg atom is coordinated by six H atoms with two Ha atoms along [110] orientation and four Hb atoms lying on (110) crystal plane, as shown in Fig. 1(a). In order to investigate the influences of strain on dehydrogenation kinetics of MgH₂, the uniaxial, biaxial and triaxial tensile/compressive strains ϵ ranging from –3% to +3% are applied to MgH₂ lattice respectively, as shown in Fig. 1(b). Then the diffusion energy barriers of Ha or Hb atom from its original site to Hb or Ha vacancy within strained MgH₂ lattice are calculated by using linear synchronous transit (LST)/quadratic synchronous transit (QST) methods [16]. To study the synergistic effects of strain and transition metal doping on dehydrogenation kinetics of MgH₂, the Nb element is chosen as the dopant and it is doped into strained MgH₂ lattice by replacing one central Mg atom, as shown in Fig. 1(c). Similar to the case of strained MgH₂, the diffusion energy barriers of Ha or Hb atom within the synergistically strained and Nb-doped MgH₂ are further calculated.

3. Results and discussions

3.1. Structural parameters

To assess the accuracy of the computational method, the

preliminary calculations on the structural parameters of strain-free MgH₂ unit cell are performed as listed Table 1. The calculated equilibrium lattice constants strain-free MgH₂ are $a = 4.6393$ Å and $c = 3.0123$ Å. The bond lengths between Mg and H atoms within MgH₂ lattice are $d_{\text{Mg-Ha}} = 2.0025$ Å and $d_{\text{Mg-Hb}} = 1.9753$ Å. These values are all in agreement with experimental and other calculated values [17–19]. In addition, the bulk modulus B_0 is calculated as 51.4474 GPa, which is also consistent with other calculated data [18]. This suggests our computations are precise to represent the ground-state properties of MgH₂.

3.2. Dehydrogenation kinetics of strained MgH₂

Generally, the kinetics of chemical reaction can be described by the Arrhenius equation [20], which gives the dependence of the rate constant k of chemical reaction on the temperature T and activation energy E_a as shown in Eq. (1):

$$k = A \exp\left(\frac{-E_a}{k_B T}\right) \quad (1)$$

where A is the pre-exponential factor and k_B is the Boltzmann constant. The applicability of the Arrhenius equation has been dealt with in some detail in the case of atomic diffusion processes, where an Arrhenius expression for the diffusion coefficient D is given by Eq. (2):

$$D = D_0 \exp\left(\frac{-E_D}{k_B T}\right) \quad (2)$$

where D_0 is the diffusion pre-exponential factor and E_D is the diffusion energy barrier. Apparently, the lower diffusion energy barrier E_D corresponds to the larger diffusion coefficient D as well as the fast diffusion kinetics at a given temperature. It is therefore necessary to determine the diffusion energy barrier E_D , which is identified as the difference in energy between the transition state (TS) and the initial state (IS) of diffusion system based on the transition state theory [21].

For MgH₂, the dehydrogenation process is complex and mainly includes H atom or vacancy diffusion, phase nucleation and growth, surface desorption, etc. [22]. Among of them, H atom diffusion in MgH₂ is an important rate-limiting step [23]. To realize H atom diffusion in MgH₂ crystal cell as shown in Fig. 1, the H vacancies need to be formed firstly through the prior desorption of some H atoms, then the nearest neighbor H atoms will diffuse from their original sites to these vacancies to realize further desorption. Thus, we firstly calculated the formation energy of Ha or Hb vacancy before simulating the H atom diffusion by using Eq. (3) [24]:

$$\Delta E_{\text{vac}} = E_{\text{tot}}(\text{Mg}_2\text{H}_3) + \frac{1}{2}E_{\text{tot}}(\text{H}_2) - E_{\text{tot}}(\text{Mg}_2\text{H}_4) \quad (3)$$

where $E_{\text{tot}}(\text{Mg}_2\text{H}_3)$ and $E_{\text{tot}}(\text{Mg}_2\text{H}_4)$ refer to the total energies of MgH₂ crystal cell with and without one Ha or Hb atom desorption respectively. $E_{\text{tot}}(\text{H}_2)$ refers to the total energy of gaseous H₂ molecule. The calculated results are plotted in Fig. 2(a). Evidently, the external strain has a marked impact on the formation energy of H vacancy. Some strains such as uniaxial tensile strain along [100] or [010] crystal direction, uniaxial compressive strain along [001] crystal direction, biaxial tensile strain within (001) crystal plane and triaxial tensile strain are all beneficial to the decreasing of H vacancy formation energy, while the others have the opposite effects. Noticeably, the formation energies of Ha vacancy in all MgH₂ models are always lower than that of Hb vacancy, suggesting preferable desorption of Ha atom lying along [110] orientation

Download English Version:

<https://daneshyari.com/en/article/5460959>

Download Persian Version:

<https://daneshyari.com/article/5460959>

[Daneshyari.com](https://daneshyari.com)