Point-defect kinetics in α - and γ -MgH₂

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Abstract

The kinetics of hydrogen desorption from storage materials in principle depend on the crystalline phase of the material. In MgH₂, desorption rates may be higher in the crystalline γ phase compared to the equilibrium bulk α phase. It has been suggested [R. A. Varin, T. Czujko, Z. Wronski, *Nanotechnol.*, 17 (15) (2006) 3856-3865] that this effect is responsible for enhanced desorption from ball-milled MgH₂, since smaller particles contain a higher proportion of the metastable γ phase. We investigate hydrogen transport kinetics in these phases of MgH₂ by using first-principles calculations based on density functional theory. Imposing charge neutrality, we find that the formation energy of hydrogen vacancies in γ -MgH₂ is smaller by 0.032 eV compared to α -MgH₂. Our calculations of migration barriers show that the only relevant point defect for mass transport in both crystal structures is the positively charged hydrogen vacancy, and that its lowest migration barrier in γ -MgH₂ is 0.02 eV lower than in α -MgH₂. We conclude that hydrogen vacancies exist in higher concentrations and are also more mobile in the γ phase than in the α phase, thus explaining the faster dehydrogenation kinetics of γ -MgH₂.

Keywords: hydrogen storage, magnesium hydride, defects, kinetics, first principles calculations

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1. Introduction

Many metal hydrides have great potential as hydrogen storage materials because they have high volumetric and gravimetric hydrogen storage capacities and can be inexpensive. However, their relatively slow hydrogen sorption kinetics in practical temperature and pressure ranges present a major obstacle to their usage, particularly in mobile applications [1]. Ball milling is a prominent technique to improve the hydrogen sorption characteristics of hydrides [2], but the mechanisms which lead to the improvement are not yet fully understood.

Magnesium hydride (MgH₂) is a prototypical hydrogen storage material that has been the subject of many experimental studies on the effect of ball milling. Huot *et al.* [3] observed that intensively ball-milled and dehydrogenated MgH₂ exhibited hydrogen absorption kinetics four times faster than unmilled material. They also found that the enhancement persisted at lower temperature and did not deteriorate by cycling at high temperature (623 K). The authors argued that ball milling leads to reduced hydride particle sizes, hence the ball-milled material exhibits an increased specific surface area, which in turn increases the nucleation site density for hydrogen sorption processes on the surface of the hydride particles. They also noted that

smaller particle sizes lead to reduced diffusion lengths for processes that take place in the bulk of the material.

Subsequent studies by Varin *et al.* [4] have indicated that the mechanisms may be more subtle. They performed controlled mechanical ball milling of commercial MgH₂ powder under hydrogen overpressure and subsequent differential scanning calorimetry (DSC) dehydrogenation, and studied the influence of both the size of the crystallites and the mean size of the hydride particles on the hydrogen desorption temperature. Commercial magnesium hydride powder consists only of the low-pressure ground-state phase α -MgH₂ (rutile crystal structure, $P4_2/mnm$). MgH₂ also has a high-pressure phase, namely γ -MgH₂ (α -PbO₂ crystal structure, $Pbcn$), and Varin *et al.* [4] found that this phase was present, along with the ground-state α phase, in powder samples that were ball milled for 10 h or longer. They found that below a certain threshold in powder particle size (≈ 500 – 600 nm), the significant drop (~ 60 °C) in the DSC onset temperature of hydrogen desorption could not be attributed solely to smaller particle dimensions. They concluded that formation of γ -MgH₂ crystallites, which is predominantly observed in the smaller powder particles, is an important contributor to the lowering of dehydrogenation temperatures in ball-milled MgH₂. The recent differential scanning calorimetric studies of Zhou *et al.* confirm that γ -MgH₂ exhibits a much lower hydrogen desorption temperature than α -MgH₂ (termed β -MgH₂ in their study) [5].

In the present study we investigate the hypothesis that

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the lower dehydrogenation temperatures can be attributed to faster hydrogen mass transport kinetics in γ -MgH₂ compared to α -MgH₂. Mass transport requires both the presence of defects and a sufficient mobility of these defects in the lattice. Native point defects govern the diffusion processes and have been established to be responsible for the kinetics of the hydrogen (de)sorption reactions in MgH₂ [6, 7, 8]. DSC studies by Novaković *et al.* [9] also showed that defects induced by ion irradiation, predominantly vacancies, significantly impact hydrogen diffusion and desorption kinetics in MgH₂.

A number of computational studies have also shown that vacancy defects are relatively abundant under dehydrogenation conditions and may thus mediate mass transport in the bulk of the hydrides. The important role of hydrogen vacancies for dehydrogenation in hydrides was confirmed in studies on AlH₃, Li amide (LiNH₂), Li imide (Li₂NH), LiBH₄ and Li₄BN₃H₁₀ [10, 11, 12, 13, 14]. It was also shown that transition metal additives in MgH₂ lower the formation energy of native defects and increase their concentration resulting in higher hydrogen desorption rates [15, 16, 17, 18]. Tao *et al.* [19] identified diffusion paths for hydrogen defects in different MgH₂ structures. They focused on the effects of deformation twins, polymorphous structure, and vacancy concentrations on migration barriers, without discussion of formation energies.

Here we will report first-principles results for the formation and diffusion of hydrogen-related defects in MgH₂, focusing on vacancy defects and on a comparison between α - and γ -MgH₂.

2. Methods

To investigate the role of defects in hydrogen transport we have determined the activation energy E_a of self-diffusion, which is the sum of the formation energy E^f and the migration barrier E_b of the corresponding defect:

$$E_a = E^f + E_b. \quad (1)$$

The formation energy of a hydrogen vacancy in charge state q in MgH₂ is defined as [20]:

$$E^f [(V_H)^q] = E_{\text{tot}} [(V_H)^q] - E_{\text{tot}} [\text{MgH}_2] + \mu_H + q\varepsilon_F, \quad (2)$$

where $E_{\text{tot}} [(V_H)^q]$ is the total energy of a supercell of the MgH₂ crystal containing the vacancy, $E_{\text{tot}} [\text{MgH}_2]$ is the total energy of the perfect crystal in the same supercell, and μ_H is the hydrogen chemical potential. ε_F is the electron chemical potential (Fermi level), which is the energy of the reservoir with which electrons are exchanged when the vacancy is in a non-neutral charge state; ε_F is referenced to the bulk valence-band maximum (VBM).

To determine the total energies and migration barriers we use density functional theory (DFT) and periodic

Figure 1: Crystallographic unit cells of (a) α -MgH₂ and (b) γ -MgH₂.

boundary conditions using the Vienna Ab initio Simulation Package (VASP) [21, 22]. The electronic wave functions are expanded in a plane-wave basis and projector augmented wave potentials are used. The crystallographic unit cells of α - and γ -MgH₂ are shown in Fig. 1. To model the defect configurations in the α - and γ -MgH₂ phases in the dilute limit [20] we used large supercells containing 96 atoms; integrations over the Brillouin zone were performed using a Γ -centered mesh.

For the exchange-correlation functional we have used the generalized gradient approximation (GGA), specifically in the Perdew-Burke-Ernzerhof (PBE) form [23]. To remove spurious contributions arising from interactions between defects and with the homogeneous compensation charge in charged supercell calculations we have applied the correction scheme of Freysoldt *et al.* [24, 25]. All equilibrium structures have been fully relaxed. The saddle points for defect migration were determined by the nudged elastic band method [26, 27].

A comparative study of defect activation energies between two different crystal structures requires high accuracy. We therefore performed detailed convergence tests. We found that an energy cutoff of 350 eV for the plane-wave basis set is sufficient to compare energy differences between supercell calculations with an accuracy of 1 meV using a $2 \times 2 \times 3$ k-point mesh for the α phase and $2 \times 2 \times 2$ k-points for the γ phase. This corresponds to 6 irreducible k-points for α - and 8 irreducible k-points for γ -MgH₂. We also performed tests with larger supercells and denser k-point meshes; we found that these changed the energy differences by less than 1 meV per unit cell. Overall, the numerical error bar of our calculations is sufficiently small, allowing us to resolve the rather delicate differences in the defect activation energies for the two phases.¹

¹“Real-space projectors” in the VASP code were deactivated. This method is intended to accelerate the determination of the projection operators by evaluating them in real space instead of reciprocal space, depending on the size of the supercell. However, we found that use of real-space projectors resulted in a small but non-negligible error of about 10 meV.

Figure 2: Calculated formation energies E^f for hydrogen vacancies in α - and γ -MgH₂ as a function of Fermi level ε_F .

3. Results

3.1. Structure

The lattice structures of α - and γ -MgH₂ are shown in Fig. 1. The calculated structural parameters for both structures (Table 1) are in good agreement with other computational results [28] as well as with experiment (obtained with x-ray diffraction (XRD) [28] as well as after structure refinement from neutron powder diffraction on the deuterides, α -MgD₂ and γ -MgD₂ [29]).

3.2. Formation energies

The calculated formation energies E^f for V_H^+ , V_H^0 and V_H^- as a function of Fermi level ε_F are plotted in Fig. 2 and shown in Table 2 for both the α and γ phase of MgH₂. Since we focus on the differences between the α and γ phase in this study, the choice of the hydrogen chemical reservoir is of no relevance. We set $\mu_H = 0$.

We observe that in both phases the neutral defect exhibits a higher formation energy than either of the charged defects (higher by 0.175 eV for α -MgH₂ and by 0.164 for γ -MgH₂). Therefore, the concentration of neutral vacancies will always be much lower than that of charged vacancies, and we do not need to consider them any further. We model pristine MgH₂, meaning that we do not consider the presence of impurities. In addition, other native defects have much higher formation energies than vacancies under H-poor conditions [8], and therefore it is legitimate to assume that charge neutrality in the sample requires that the V_H^+ and the V_H^- defects must exist in equal concentrations and hence must have the same formation energy.

Imposing charge neutrality therefore pins the Fermi level to 2.808 eV in α -MgH₂, with $E^f(V_H^+) = E^f(V_H^-) = 1.428$ eV. In γ -MgH₂ the Fermi level is pinned at 2.618 eV, and the formation energies of the vacancies are $E^f(V_H^+) = E^f(V_H^-) = 1.396$ eV. The formation energy E^f for charged

Table 2: Calculated formation energies E^f for charged and neutral hydrogen vacancies V_H , calculated migration barriers $E_b(1)$, $E_b(2)$, and $E_b(3)$ along the different diffusion paths for positively and negatively charged hydrogen vacancies V_H , and resulting activation barriers $E_a(1)$, $E_a(2)$, and $E_a(3)$ in α - and γ -MgH₂. For the α phase, paths 2 and 3 are equivalent. All values in eV.

	α -MgH ₂	γ -MgH ₂
$E^f(V_H^0)$	1.603	1.560
$E^f(V_H^+) = E^f(V_H^-)$	1.428	1.396
$V_H^+ E_b(1)$	0.372	0.367
$V_H^+ E_b(2)$	0.389	0.414
$V_H^+ E_b(3)$	0.389	0.350
$V_H^- E_b(1)$	1.723	1.512
$V_H^- E_b(2)$	1.135	1.110
$V_H^- E_b(3)$	1.136	1.547
$V_H^+ E_a(1)$	1.800	1.763
$V_H^+ E_a(2)$	1.817	1.810
$V_H^+ E_a(3)$	1.817	1.746
$V_H^- E_a(1)$	3.151	2.908
$V_H^- E_a(2)$	2.563	2.506
$V_H^- E_a(3)$	2.564	2.943

vacancies is therefore smaller by 0.032 eV in γ -MgH₂ compared to α -MgH₂. Our first important conclusion is therefore that, due to their lower formation energy, charged vacancies are present in higher concentrations in γ -MgH₂ in comparison to α -MgH₂.

3.3. Migration barriers

For both α - and γ -MgH₂ the hydrogen atoms are positioned in octahedral coordination around the Mg atoms (Fig. 3). However, depending on the lattice parameters and the lattice symmetry of the host lattice, the octahedra are squeezed along one (in the case of α -MgH₂) or two (in the case of γ -MgH₂) axes. From the symmetry considerations we can deduce that in γ -MgH₂ three inequivalent paths exist for the migration process [labeled with $\gamma 1$, $\gamma 2$, and $\gamma 3$ in Fig. 3 (b)], whereas in α -MgH₂ only two inequivalent paths (labeled with $\alpha 1$ and $\alpha 2$) exist [Fig. 3 (a)].

The calculated migration barriers along these diffusion paths are shown in Table 2, for both V_H^+ and V_H^- . In both phases, the positively charged hydrogen vacancy V_H^+ has much lower diffusion barriers than the negatively charged vacancy. For that reason, the positively charged hydrogen vacancy will be the only relevant point defect for mass transport in both crystal structures.

The potential energy surfaces for migration along the various paths are shown in Fig. 4. The different possible paths lead to barrier heights that differ by less than 0.02 eV in α -MgH₂, but by more than 0.06 eV in γ -MgH₂. Overall, the lowest migration barrier in γ -MgH₂ is more than 0.02 eV lower than the smallest value for α -MgH₂ (Table 2).

Table 1: Comparison of calculated and experimentally observed structural data of α -MgH₂ ($P4_2/mnm$) and γ -MgH₂ ($Pbcn$). Lattice parameters a , b , and c as well as the H–Mg distances $d(\text{H–Mg})$ are given in Å. Reference [29] reported neutron powder diffraction (NPD) data for the respective deuterides (α -MgD₂ ($P4_2/mnm$) and γ -MgD₂ ($Pbcn$)). The H–Mg distances $d(\text{H–Mg})$ calculated using DFT by Vajeeston *et al.* [28] were derived using theoretically calculated positional parameters together with experimentally derived unit-cell dimensions and thus differ slightly from the values calculated in this work.

	a	b	c	$d(\text{H-Mg})$		
$\alpha\text{-MgH}_2$						
This work	4.4867	4.4867	2.9998	1.9297	1.9479	1.9479
Ref. [28] DFT	4.4853	4.4853	2.9993	1.944	1.961	1.961
Ref. [28] XRD	4.5176	4.5176	3.0206			
Ref. [29] NPD	4.5010(1)	4.5010(1)	3.0100(1)	1.9351(9)	1.9549(6)	1.9549(6)
$\gamma\text{-MgH}_2$						
This work	4.4861	5.4028	4.8978	1.9053	1.9410	1.9952
Ref. [28] DFT	4.4860	5.4024	4.8985	1.920	1.955	2.011
Ref. [28] XRD	4.5246	5.4442	4.9285			
Ref. [29] NPD	4.5051(2)	5.4197(2)	4.9168(2)	1.915(3)	1.943(3)	2.004(3)

Figure 3: MgH₆ octahedra and nomenclature of the respective migration paths in (a) α - and (b) γ -MgH₂. For the α phase, paths 2 and 3 are equivalent.

Figure 4: Potential energy surfaces for migration of V_{H}^+ along different paths in α - and γ -MgH₂. For the α phase, paths 2 and 3 are equivalent.

3.4. Activation energies

We can now put the results of the previous two sections together. V_{H}^+ point defects, which are most relevant for the mass transport effects in bulk-MgH₂ during the dehydrogenation process, exist in higher concentrations (Sec. 3.2) and are more mobile (Sec. 3.3) in the γ phase than in the α phase. To quantify these effects, we calculate the activation energy of thermally activated self-diffusion E_a according to Eq. (1) (Table 2). The lowest activation barrier E_a for γ -MgH₂ (corresponding to path 3) is 0.05 eV smaller than the lowest barrier for α -MgH₂ (path 1).

Hydrogen diffusion mediated by positively charged hydrogen vacancies can therefore proceed more easily in γ - than in α -MgH₂. This confirms the suggestion [4] that the differences between α - and γ -MgH₂ contribute to the lower observed dehydrogenation onset temperature of ball-milled MgH₂ with smaller particle sizes (which contained a higher proportion of the γ phase).

We can quantify the effect of a difference in activation barriers of 0.05 eV on reaction rates and desorption temperatures by applying transition state theory. If the dehydrogenation reaction takes place at 300 °C, a difference of 0.05 eV in the activation energy E_a leads to an increase in reaction rate by a factor of three. Conversely, a 0.05 eV difference in activation energy corresponds to a decrease in desorption onset by 15 °C. These differences are of a magnitude that is consistent with the effects observed by Varin *et al.* [4].

We can attribute the observed differences in point-defect formation energies and migration barriers to specific differences in the structure and the lattice parameters of the two phases. The crystal structures include MgH₆ octahedra for both α - and γ -MgH₂ (Fig. 3). While the MgH₆ octahedron is only slightly squeezed along the axial bonds in α -MgH₂, it is heavily distorted in γ -MgH₂. The differences in Mg–H bond lengths (Table 1) are consistent with the differences in calculated diffusion barriers for the various V_{H} migration paths (Table 2).

α - and γ -MgH₂ differ only in their respective symmetry ($P4_2/mnm$ and $Pbcn$) but possess the same stoichiometry. Differences in point-defect formation energies therefore originate from structural differences. The average value for the H-Mg distances is 1.9418 Å in α -MgH₂ and 1.9472 Å for γ -MgH₂. We suggest that this greater distance between Mg and H reduces the Coulomb attraction, thus lowering the formation energy and facilitating H motion atom in γ -MgH₂ compared to α -MgH₂.

4. Summary

Positively charged hydrogen vacancies V_H^+ exist in a higher concentration and are more mobile in γ -MgH₂ in comparison to α -MgH₂. The faster dehydrogenation kinetics of nanocrystalline MgH₂ powders, as observed by Varin *et al.* [4], can therefore be attributed at least in part to a lowering of diffusion activation barriers for hydrogen-related point defects in the γ phase.

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