Point-defect kinetics in α- and γ-MgH$_2$

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ABSTRACT

The kinetics of hydrogen desorption from storage materials in principle depend on the crystalline phase of the material. In MgH$_2$, 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 MgH$_2$, since smaller particles contain a higher proportion of the metastable γ phase. We investigate hydrogen transport kinetics in these phases of MgH$_2$ by using first-principles calculations based on density functional theory. Imposing charge neutrality, we find that the formation energy of hydrogen vacancies in γ-MgH$_2$ is smaller by 0.032 eV compared to α-MgH$_2$. 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-MgH$_2$ is 0.02 eV lower than in α-MgH$_2$. 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-MgH$_2$.

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 (MgH$_2$) 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 MgH$_2$ exhibited hydrogen absorption kinetics four times faster then 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, P4/2mnm). 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 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 [6–8]. 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 [10–14]. 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 [15–18]. 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.

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:

$$E_a = E^f + E_b. \tag{1}$$

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

$$E^f\left[(V_H)^q\right] = E_{tot}\left[(V_H)^q\right] - E_{tot}\left[MgH_2\right] + \mu_H + q\varepsilon_F, \tag{2}$$

where $E_{tot}[(V_H)^q]$ is the total energy of a supercell of the MgH₂ crystal containing the vacancy, $E_{tot}[MgH_2]$ 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 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
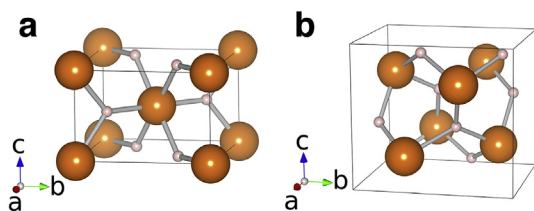

Fig. 1 – Crystallographic unit cells of (a) α-MgH₂ and (b) γ-MgH₂.