

## Effect of transition-metal additives on hydrogen desorption kinetics of MgH<sub>2</sub>

Anindya Roy, Anderson Janotti, and Chris G. Van de Walle Materials Department, University of California, Santa Barbara, California 93106-5050, USA

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Using first-principles calculations, we study the effect of transition-metal additives (Ti, Fe, Co, and Ni) on the rate of hydrogen desorption in MgH<sub>2</sub>. The presence of large concentrations of transition-metal impurities causes the Fermi level to shift according to the position of the transition-metal acceptor/donor levels in the band gap. This shift can lower the formation energy of native defects and increase their concentration. The resulting higher rates of hydrogen desorption enhance the prospect of MgH<sub>2</sub> as a solid-state hydrogen-storage material. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4788746]

Hydrogen storage is an important piece of the challenge in moving towards a hydrogen economy, away from the present carbon-based economy.<sup>1,2</sup> Reversible solid-state hydrogen storage systems based on metal hydrides have been receiving a fair amount of attention in this regard, MgH<sub>2</sub> being a prominent candidate. MgH<sub>2</sub> has good gravimetric and volumetric hydrogen-storage capacity,<sup>1</sup> but the temperature of hydrogen desorption,  $T_{des}$ , at 350 °C or higher<sup>3</sup> is beyond the useful range for automotive applications.

The decomposition reaction of MgH<sub>2</sub> into metallic Mg and H<sub>2</sub> gas is primarily governed by the Gibbs free energy ( $\Delta G$ ) of the process, which is a function of temperature and pressure. Thermodynamics would allow the dehydrogenation reaction to proceed at a temperature of 280 °C or higher at standard atmospheric pressure.<sup>4</sup> In reality, the reaction is extremely slow at the above temperature, and requires the temperature to be raised by 100 °C or more for an acceptable rate of hydrogen desorption. This higher temperature requirement must be attributed to kinetic barriers, which could be lowered by appropriate additives. We note that there is no expectation that such additives would lead to an appreciable change in the thermodynamics, i.e., a reduced formation enthalpy of MgH<sub>2</sub>.

Indeed, it has been found that the addition of small quantities (1–5 at. %) of transition metals (TM), such as Fe, Co, Ni, Ti, Nb, or Zr, brings down  $T_{des}$  and enhances the kinetics of the process.<sup>3,5–10</sup> Practical issues make it difficult to pinpoint the mechanism by which transition metals influence the reaction. These issues include variations in the amount of impurities added, details of the physical and chemical states of the reactants resulting from ambient conditions (such as hydrogen partial pressure), and process of synthesis (such as duration and details of ball-milling process, and condition of the initial sample). An understanding of the mechanism is of critical importance, however, to improve the process and to identify more efficient additives.

It has been suggested that the observed enhancements could be due to formation of compound phases such as  $Mg_2Fe$ -hydride or  $Mg_2Ni$ -hydride;<sup>11,12</sup> however, the fact that the effects are observed at relatively low concentrations of the TM impurities (5 at. % or even lower) suggests a different mechanism, based on modification of the properties of bulk MgH<sub>2</sub>. Native point defects, such as vacancies and interstitials, govern the diffusion processes that lead to

formation of MgH<sub>2</sub> from metallic Mg and H<sub>2</sub> gas, and dehydrogenation of MgH<sub>2</sub> back into Mg and H<sub>2</sub>. Such defects are thus believed to be responsible for the kinetics of the hydrogen (de)sorption reactions.<sup>13–15</sup> The activation energy for dehydrogenation is then given by the sum of the formation energy and the migration barrier of the defect responsible for H mass transport.

In wide-band-gap insulators such as MgH<sub>2</sub>, free carriers are not present, and defects exist in charged states. The Fermi level is determined by having equal concentrations of oppositely charged defects according to the charge neutrality condition. In the absence of impurities, the Fermi level is pinned close to a position in the gap where the formation energy of the dominant negatively charged native defect equals that of the dominant positively charged defect. In the present work, we investigate the effects of adding transition metal impurities on the dehydrogenation kinetics in MgH<sub>2</sub>. We find that transition-metal impurities in MgH<sub>2</sub> have the effect of shifting the Fermi level away from the position in the intrinsic material, thus, lowering the formation energy of defects that are responsible for H transport. Such an effect, previously discussed in the context of other metal hydrides,<sup>16–19</sup> is explored here for Ti, Fe, Co, and Ni additives in MgH<sub>2</sub>.

Our calculations are based on density functional theory with the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)<sup>20,21</sup> as implemented in the Vienna Ab initio Simulation Package (VASP) code.<sup>22,23</sup> The amount of exact exchange admixed with the generalized gradient functional in the HSE approach was set to 33%, resulting in a calculated band gap of 5.2 eV, close to the lower limit of experimentally observed band gaps.<sup>24</sup> We verified that using the "standard" value of 25%, exact exchange does not alter any of the physical conclusions obtained in this work, although the corresponding band gap is smaller (4.8 eV). The calculated lattice constants a = 4.45 Å and c = 2.99 Å, along with the structure parameter u = 0.304 for bulk MgH<sub>2</sub> in the rutile crystal structure, are in very good agreement with the experimental values of 4.51 Å, 2.99 Å, and 0.304, respectively.<sup>25</sup> The defect calculations were performed for a supercell containing 72 atoms, which is a  $2 \times 2 \times 3$  repetition of the primitive cell. A mesh of  $2 \times 2 \times 2$  special k-points and an energy cutoff of 270 eV for the plane-wave basis set were used for the defect-containing supercells. Charged defects are treated based on the formalism described in Ref. 26, by changing the number of electrons in the supercell and verifying that the states which electrons are added to or removed from are localized on the impurity. A compensating background charge prevents divergence of the total energy, and finitesize supercell effects were corrected following the method developed by Freysoldt *et al.*<sup>27,28</sup> The effects of spin polarization were also included.

The concentration of a defect X at temperature T is given by  $^{26}$ 

$$C(X) = N_{\text{sites}} N_{\text{config}} \exp\left(-\frac{E^{\text{f}}}{kT}\right),\tag{1}$$

where  $N_{\text{sites}}$  is the number of sites per unit volume that can accommodate the defect, and  $N_{\text{config}}$  is the number of configurations per site. The formation energy  $E^{\text{f}}$  of a native defect X in the charge state q is obtained from

$$E^{\rm f}(X^q) = E_{\rm tot}(X^q) - E_{\rm tot}^{\rm bulk} - \sum_i n_i(\mu_i + E_{{\rm ref},i}) + qE_{\rm F},$$
 (2)

where  $E_{tot}(X^q)$  and  $E_{tot}^{bulk}$  are the total energies of the supercell with the defect in charge state q and that of the defectfree bulk.  $E_{\rm F}$  represents the Fermi level, referenced to the valence-band maximum (VBM) of the host material. The number of atoms of a species added or subtracted is given by a positive or negative value of  $n_i$ . The  $\mu_i$  values, finally, are the chemical potentials of species *i*, referenced to  $E_{\text{ref},i}$ . The latter corresponds to the energy per atom of bulk Mg  $(E_{\rm ref,Mg})$ , or half the total energy of a hydrogen molecule  $(E_{\rm ref,H_2})$ .  $\mu_i$  is a variable dependent on conditions of pressure and temperature; in equilibrium, stability of MgH2 requires that  $\mu_{Mg} + 2\mu_{H} = \Delta H_f(MgH_2)$ , with  $\mu_{Mg} \leq 0$  and  $\mu_{H} \leq 0$ .  $\Delta H_{\rm f}({\rm MgH_2})$  is the formation enthalpy of bulk MgH<sub>2</sub>. For the hydrogen desorption reaction, H-poor (Mg-rich) conditions are most relevant, corresponding to  $\mu_{Mg} = 0$  and  $\mu_{\rm H} = 1/2\Delta H_{\rm f}({\rm MgH}_2).$ 

The formation energy curves also contain useful information about the relative stability of different charge states for a specific impurity. The Fermi-level positions that mark the transition between charge states  $q_1$  and  $q_2$ , i.e., the charge-state transition levels  $\varepsilon(q_1/q_2)$ , delineate the energy regions over which particular charge states are stable. The usual ordering is  $\varepsilon(+/0) < \varepsilon(0/-)$ , reflecting a positive repulsion energy U when electrons are added. Sometimes, however,  $\varepsilon(0/-) < \varepsilon(+/0)$ , a situation that is referred to as "negative-U" and is related to large differences in lattice relaxations between different charge states. In that case, the transition occurs directly from the + to the - charge state as a function of Fermi level, and the relevant transition level is  $\varepsilon(+/-)$ .

The formation energies of native point defects as a function of Fermi level under H-poor conditions are shown in Fig. 1, and Table I contains the formation-energy values at  $E_F^{int}$ . Taking all the defects into account and applying Eq. (1), we find that the intrinsic Fermi level at which overall charge neutrality is satisfied occurs at  $E_F^{int} = 3.84 \,\text{eV}$ . Hydrogen vacancies are the lowest energy defects at this Fermi level.

Overall, our present results for native defects are in good agreement with the previous study by Park *et al.*<sup>15</sup> The



FIG. 1. Formation energies of native point defects in bulk  $MgH_2$  in different charge states as a function of Fermi level under H-poor conditions. The vertical solid line indicates the intrinsic Fermi level.

relaxed structures of hydrogen vacancies, the dominant defects, are very similar to those found by Park *et al.* (to within 0.02 Å). Some quantitative differences do occur, however, and they can be attributed to two causes. First, in our present study, we find that  $V_{\rm H}$  shows a positive-*U* behavior,  $V_{\rm H}^0$  being the lowest-energy defect in the range of Fermi levels between 3.5 eV and 4.1 eV, with a formation energy of 0.96 eV. This contrasts with the results of Ref. 15, where  $V_{\rm H}$  was found to be a negative-*U* center in which  $V_{\rm H}^0$  is never the lowest-energy charge state for any Fermi-level position. The difference is due to the inclusion of spin polarization in the present work, lowering the energy of the neutral charge state which contains an unpaired electron. We find that including spin-polarization lowers the formation energy of the neutral vacancy by 0.4 eV.

The second difference with the results of Park et al.<sup>15</sup> occurs in the overall values of formation energies, and is related to the fact that in the present study the HSE hybrid functional is used, whereas the previous work used a generalized gradient approximation (GGA) functional. The HSE hybrid functional lowers the energy of the valence band on an absolute energy scale, an effect we can quantify by performing a surface calculation using a slab of MgH<sub>2</sub> in a nonpolar [110] orientation. In the GGA calculation the VBM occurs at 6.72 eV below the vacuum level, while in HSE, the VBM is lowered by 1.06 eV, to a position 7.78 eV below the vacuum level. This shift in the VBM is largely responsible for the differences in absolute formation energies between the present HSE results and the previous GGA results.<sup>15</sup> However, we emphasize that even though using HSE significantly changes the band gap and absolute formation energies at the VBM, the relevant quantities, which are the formation

TABLE I. Formation energies (in eV) of native point defects at  $E_F^{int}$  in different charged states.

	Formation energy (eV) in charge state $q$				
Defect	-2	-1	0	+1	+2
$V_{\rm H}$		1.25	0.96	1.25	
$H_i$		1.52	2.75	2.01	
H <sub>2i</sub>	3.44	3.63	2.07	4.50	4.15
$V_{Mg}$	1.76	4.49	5.31	6.01	5.69
Mgi	6.81	6.14	4.04	2.64	1.92



FIG. 2. Formation energies of TM impurities in  $MgH_2$  in different charge states, as a function of Fermi level under H-poor condition. Interstitial configurations of (a) Ti, (b) Co, (c) Fe, and (d) Ni are shown. The vertical dashed line refers to the intrinsic Fermi level.

energies in the vicinity of the intrinsic Fermi level, differ by less than 0.2 eV between GGA and HSE.

Next, we examine the effect of TM impurities. The formation energies of interstitial and substitutional impurities as a function of Fermi level are shown in Figs. 2 and 3. The intrinsic Fermi level is indicated by the vertical dashed line in each panel. We note that the absolute formation energies for the TM impurities should not be used to calculate concentrations using Eq. (1). Indeed, this expression is only valid close to equilibrium, and the conditions (such as ball milling) under which the TM impurities are introduced into hydrogen storage materials tend to be far from equilibrium. In addition, diffusion barriers for these impurities tend to be much higher than for the native point defects discussed above,<sup>15</sup> again indicating that incorporation is not governed by an equilibrium process. Qualitatively, however, the formation energies can still provide an indication of which impurities or configurations are more likely to be incorporated.

To understand how the presence of TM impurities alters the concentration of native defects by shifting the Fermi level, we discuss different cases depending on the location of the



FIG. 3. Formation energies of TM impurities in  $MgH_2$  in different charge states, as a function of Fermi level under H-poor condition. Substitutional configurations (on the Mg site) of (a) Ti, (b) Co, (c) Fe, and (d) Ni are shown. The vertical dashed line refers to the intrinsic Fermi level.

charge-state transition levels of the TM impurity vis-à-vis the intrinsic Fermi level,  $E_F^{int}$ .<sup>29</sup> Here, we assume that the concentration of the TM impurities dispersed in the host materials is much higher than that of native defects. The Fermi-level position will then be determined by the lowest-energy charge states of the TM impurity through the charge-neutrality condition. If the TM impurity exhibits a negative-U character, the Fermi level will coincide with  $\varepsilon(+/-)$ , and the shift in  $E_F$  induced by the TM impurity is given simply by  $\varepsilon(+/-) - E_F^{int}$ . If the TM impurity has positive-U character, we need to consider three distinct cases: (i)  $E_F^{int} < \varepsilon(+/0)$ ; (ii)  $\varepsilon(+/0) < E_F^{int} < \varepsilon(0/-)$ ; and (iii)  $E_F^{int} > \varepsilon(0/-)$ . In case (i), charge neutrality is determined by the positively charged TM impurity and a negatively charged H-related defect, and an upward shift of  $E_F$  will occur. In case (iii), charge neutrality is determined by the negatively charged TM impurity and a positively charged H-related defect, leading to a downward shift of  $E_F$ . In case (ii), the TM effect is unlikely to have any effect, since it is stable in the neutral charge state over a range of Fermi levels that includes  $E_F^{int}$ , and hence no TM-induced shift in  $E_F$  is expected.

If the addition of a TM brings down the formation energy of hydrogen-related defects, their concentration may increase by many orders of magnitude. Given their small migration barrier,<sup>15</sup> this would lead to significant enhancement of kinetics and lowering of desorption onset temperature compared to undoped samples.

With this understanding, we examine the various TM impurities, starting with the interstitial defects. Figure 2(b) shows that  $Co_i$  has negative-*U* character and would lead to a distinct upward shift in  $E_F$ . Ti<sub>i</sub> and Fe<sub>i</sub> correspond to case (i) described above, in which an upward shift of  $E_F$  may occur, though the effect would be modest for Fe<sub>i</sub>. Ni<sub>i</sub>, finally, lies at the border between cases (i) and (ii); a detectable effect may occur. For Ti<sub>i</sub>, Fe<sub>i</sub>, Co<sub>i</sub>, and possibly for Ni<sub>i</sub>, an increase in the concentration of negatively charged H-related defects would occur.

Figure 3 shows that the substitutional TM impurities all have positive-*U* character, with  $Ti_{Mg}$ ,  $Fe_{Mg}$ , and  $Ni_{Mg}$  corresponding to case (ii), where no Fermi-level shift is expected. We observe, though, that  $Fe_{Mg}$  and  $Ni_{Mg}$  are borderline cases where an effect cannot be excluded.  $Co_{Mg}$  is a clear example of case (iii), where a downward shift in  $E_F$  will lead to an increase in positively charged H-related defects.

We now discuss published experiments in light of our computational results. All four TM additives considered here have been found to have some effects in dehydrogenation experiments. Addition of about 5 at. % Ti,<sup>5,10</sup> Co,<sup>8</sup> or Fe<sup>5,6</sup> all lead to an improvement in kinetics. For Ti and Fe, this could be due to interstitials [Figs. 2(a) and 2(c)], while for Co both interstitials and substitutionals could play a role [Figs. 2(b) and 3(b)].

Adding 0.5 at. % of Ni does not improve the kinetics, but adding 2 at. % does.<sup>3</sup> Increasing the concentration level of Ni in the range of 2–5 at. % shows no further improvement, while 10 at. % Ni shows drastically different behavior.<sup>7</sup> Our results show that we expect no effect for Ni<sub>*i*</sub> [Fig. 2(d)], while Ni<sub>Mg</sub> [Fig. 3(d)] is a borderline case, which may explain why fairly large concentrations are needed before an effect is observed, experimentally.

Our first-principles calculations are therefore consistent with the experimental observations and can explain the mechanism by which adding TM impurities enhances kinetics, namely through increasing the concentration of point defects responsible for hydrogen diffusion. Various experiments have indeed shown a decrease in desorption temperature  $T_{des}$  by as much as 50 °C.<sup>3,5–10</sup> The decrease in  $T_{des}$  is limited by thermodynamics. As the desorption temperature goes down, we approach the thermodynamically determined minimum temperature from above, and this enhances the rate of the backward reaction, partially offsetting the advantages of being able to lower  $T_{des}$ .

In summary, we have examined the effect of Ti, Fe, Co, and Ni impurities on the kinetics of hydrogen desorption in MgH<sub>2</sub>. All of these impurities, in either interstitial or substitutional configurations, cause a shift in the Fermi level, which in turn enhances the concentration of the hydrogen vacancies that govern hydrogen diffusion. This mechanism provides an explanation for the enhanced rate of dehydrogenation that has been experimentally observed upon addition of transition-metal impurities to MgH<sub>2</sub>.

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