Understanding of hydrogen desorption mechanism from defect point of view

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Widespread adoption of hydrogen for vehicle applications critically depends on the discovery of solid materials to store hydrogen with high volumetric and gravimetric densities, as well as to extract and insert it at sufficiently rapid rates. Complex hydrides (such as NaAlH₄, LiAlH₄, LiBH₄, Ca(BH₄)₂, Li₄BN₃H₁₀ and Li₄BN₃H₁₀), light metal hydrides of MgH₂ and AlH₃ and ammonia borane (NH₃BH₃) have recently received considerable attention as potential hydrogen storage materials due to their high hydrogen gravimetric capacity as well as volumetric capacity. However, all of these materials suffer from unfavorable dehydrogenation thermodynamics and/or slow dehydrogenation kinetics, limiting their practical applications. Yet, the harsh and ill-controlled dehydrogenation process might be overcome eventually by carefully controlling and catalyzing the hydrogen release process, calling for an in-depth understanding of dehydrogenation mechanisms.

Dehydrogenation in the above-mentioned materials involves the bond-breaking process and migration of constituent atoms, which can be accomplished through the creation and subsequent diffusion of some native point defects. Furthermore, native point defects may also serve as nucleation sites for new phases that are formed in the process of dehydrogenation reactions. Thus a deep understanding of the nature of point defects is necessary. Computational studies based on density functional theory (DFT) play an important role in defect-related properties and may help to understand the details of the hydrogen release process at the atomic level. In this perspective, we provide information about point defects to understand the dehydrogenation properties of hydrogen storage materials with a band gap. The defect properties in metallic hydrogen storage materials [1] are not within the scope of this brief review. Prof. Van de Walle’s group from the University of California, Santa Barbara, has done some pioneering computational work on point defects in NaAlH₄ [2,3]. Since this work, the properties of defects, especially H-related defects, in Na₃AlH₆ [4], LiAlH₄ [5], LiBH₄ [6], Li₄BN₃H₁₀ [6–8], LiNH₂ [9,10], MgH₂ [11,12] and AlH₃ [13] have been investigated computationally.

One key quantity in defect physics is the formation energy for the defect. According to the formation energies of defects, it is possible to find out which kinds of defects are predominant in lattices. The above-mentioned hydrogen storage materials are classified as insulators with wide band gaps; thus, the point defects in the lattice may be in charged states and the formation energies are Fermi-level dependent. In first-principles calculations, the defect is usually surrounded by a few dozen to a few hundred atoms, i.e. the so-called supercell approach. For a defect with a charge q (including its sign), its formation energy $E_f$ is given by [14]

$$E_f(X^q) = E(X^q) - E_{\text{bulk}} - \sum_{i} n_i \mu_i + q(E_V + \varepsilon_F) + E_{\text{corr}},$$

where $E(X^q)$ and $E(\text{bulk})$ denote the total energies of the supercell containing a defect $X$ in the charged state $q$ and of the defect-free supercell, respectively. $n_i$ indicates the number of atoms of type $i$ (host atoms or impurities) that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell upon defect creation, and $\mu_i$ are the corresponding chemical potentials of these species, which represent the energy of the reservoirs with which atoms are being exchanged. $\varepsilon_F$ is the chemical potential of the electrons or Fermi level, which accounts for exchanging electrons with an electron reservoir. $E_V$ is conventionally taken with respect to the valence band maximum (VBM) of the perfect lattice and can vary.
from VBM to conduction band minimum (CBM). The last term of equation (1) is a correction term that accounts for the electrostatic interactions between supercells [14]. As shown in equation (1), the formation energies of defects depend on the atomic chemical potentials and the Fermi level. The chemicals reflect the reservoirs for atoms that are involved in creating the defect. The dehydrogenation conditions under which the defects are created uniquely define the relevant reservoirs. So the chemical potentials can be determined by local equilibrium conditions in the dehydrogenation. For example, the first step of desorption of NaAlH₄ is:

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2. \tag{2}
\]

The local equilibrium conditions for dehydrogenation of NaAlH₄ could be (i) equilibrium with NaAlH₄, Na₃AlH₆ and Al; (ii) equilibrium with NaAlH₄, Na₃AlH₆ and H₂; or (iii) equilibrium with NaAlH₄, Al and H₂ [3]. For equilibrium condition (i), we have:

\[
3\mu_{\text{Na}} + \mu_{\text{Al}} + 6\mu_{\text{H}} = \mu_{\text{NaAlH}_4}. \tag{3}
\]

\[
\mu_{\text{Al}} = \mu_{\text{Al}}^0, \tag{5}
\]

where the chemical potentials of \(\mu_{\text{NaAlH}_4}\) and \(\mu_{\text{NaAlH}_6}\) are the free energy of a formula unit of NaAlH₄ and Na₃AlH₆, respectively. \(\mu_{\text{Al}}^0\) is the chemical potential of Al in its standard state. By solving equations (3)–(5) the chemical potentials of Na, Al and H under condition (i) can be obtained. More details on the discussion of chemical potentials can be found in [3,8].

First-principles calculations have indicated that H-related point defects in NaAlH₄ [2], LiAlH₄ [5], LiBH₄ [6], Li₄BN₃H₁₀ [6,7], LiNH₂ [9,10], MgH₂ [11,12], AlH₃ [13] and NH₃BH₃ are charged, and the neutral H vacancy or interstitial is higher in energy than the corresponding charged one. Figure 1 shows the formation energy of H-related defects in NaAlH₄, and Table 1 summarizes the predominant H-related defects in some novel hydrogen storage materials. The formation energies of charged H-related defects in the above materials are Fermi-level dependent; thus hydrogen release kinetics may be adjusted by adding electrically active impurities to shift the equilibrium position of the Fermi level determined by the condition of charge neutrality [2,14]. It has been found that [2] adding Zr impurity to NaAlH₄ has a tiny effect on the formation energies of H-related defects, but incorporation of a small fraction of Ti in it can result in shifting the Fermi level from its equilibrium value in intrinsic material by 0.44 eV. Correspondingly, this shift makes the formation energy of the predominant H-related point defect of H⁺ decrease by 0.44 eV. This finding might account for the observation of the improved hydrogen release kinetics in experiment when Ti-based species were ball-milled with NaAlH₄. The role of impurities in LiBH₄, Li₄BN₃H₁₀, MgH₂ and NaMgH₃ on hydrogen release has also been addressed in the literature [6,15]. Another important issue related to hydrogen release is the diffusion of defects, especially for the diffusion barrier. The diffusion barriers for the predominant defects can be directly obtained by the nudged elastic band (NEB) method or the dimer method. For NaAlH₄, the dominant H-related defects are V⁺ and H⁻. The calculated diffusion barriers for V⁺ and H⁻ are substantially low (0.26 eV for V⁺ and 0.22 eV for H⁻) [2]. The substantially low value of the diffusion barriers indicates that defect migration is not a rate-limiting step for self-diffusion of hydrogen, and that the formation of

Table 1. Summary of the predominant H-related defects in some novel hydrogen storage materials. \(V_i^+\): positive H vacancy, \(V_i^-\): negative H vacancy, \(H_i^+\): positive H interstitial and \(H_i^-\): negative H interstitial.

| Compound   | Predominant defects | Comment                                      |
|------------|---------------------|----------------------------------------------|
| NaAlH₄ [3] | \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | Equilibrium with NaAlH₄, Na₃AlH₆ and Al       |
| LiAlH₄ [5] | \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | Equilibrium with LiAlH₄, Li₃AlH₆ and Al       |
| LiNH₂ [9,10]| \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | Equilibrium with LiNH₂, LiH and Li₂NH or with LiNH₂, Li₃NH and H₂ |
| LiBH₄ [6]  | \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | Equilibrium with LiBH₄, LiH and B             |
| Li₄BN₃H₁₀ [6]| \(H_{\text{H}}^+\) and \(H_{\text{H}}^-\) | Equilibrium with Li₄BN₃H₁₀, Li₃BN₂, Li₃NH and NH₃ |
| ammonia borane | \(V(H_{\text{H}}^+)\) and \(V(H_{\text{H}}^-)\) | Equilibrium with NH₃BH₄, NH₃ and H₂ or with NH₃BH₄, B₂H₆ and H₂ |
| NaMgH₃ [15]| \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | H-rich condition                             |
| MgH₂ [11]  | \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\) | H-rich condition                             |
| AlH₃ [13]  | \(V_{\text{H}}^+\) and \(V_{\text{H}}^-\) | H-poor condition                             |

Figure 1. Formation energies vs Fermi level for H-related defects in NaAlH₄. It shows that the dominant H-related defects are \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\). The vertical line denotes the intrinsic equilibrium Fermi-level position determined by charge neutrality. If exotic charged defects are present in the host material and the concentrations exceed those of native charged defects, the Fermi-level position will shift and, accordingly, lead to change in the formation energy of \(V_{\text{H}}^+\) and \(H_{\text{H}}^-\). Reproduced with permission from Ref [2].
H-related defects is the key step in dehydrogenation. The diffusion barriers for the dominant H-related defects in LiNH2 were calculated to be 0.88 eV for V_{H^i} and 0.46 eV for H^+ [9]. At equilibrium conditions, the formation energies of V_{H^i} and H^+ are, respectively, 0.68 eV and 1.49 eV [9]. So it is fair to say that the equilibrium concentration of H interstitial is low and the formation of H interstitial is the bottleneck for H transport. Thus, the key strategy for improving the hydrogen desorption kinetics of LiNH2 is to enhance the concentration of H interstitial. This can be achieved by a nonequilibrium process such as mechanical ball milling and irradiation. The migration of H-related defects in MgH2 and LiBH4 can be found in [6,11,12].

In addition to formation energies and diffusion barriers for defects, it is equally important to inspect the local lattice structure associated with the creation of point defects. The information about local lattice structure not only indicates how the point defects cause perturbations in the lattice, but may also account for why some byproducts or intermediates are formed in hydrogen desorption reactions. In LiBH4 [6], the V_{H^i} results in formation of a BH3 unit, and H^+ leads to a BH3 unit and an H2 molecule. The BH3 units could combine and form the gas phase of diborane (B2H6), which may be emitted during the dehydrogenation process. This may explain the unrecoverable loss of boron in experiments. The creation of H^0 or H^+ in LiNH2 leads to the formation of an NH3 unit [9,10]. Formation of the NH3 unit can account for the experimentally confirmed generation of the NH3 molecule in the dehydrogenation of LiNH2. Our recent first-principles calculations on native defects in ammonia borane show that the creation of positive H vacancy in BH3 unit [V(HB^3 +)] and negative H interstitial (H^−) results in highly reactive species of [BH3]^3− and [BH4]^− (see Fig. 2), respectively. Due to the Coulomb interaction between the positive [BH3]^3− unit and negative H atoms in the nearby BH3 unit, V(HB^3 +) results in formation of an NH3BH2–H–BH2NH3 complex. The [BH3]^3− could also react with [NH2]^−, which is generated associated with creation of V(NH3^−), to form linear NH3BH2–NH2BH3, which was proposed to form in the first stage of thermal decomposition of NH3BH3 in experiment. The two reactive species may combine with other charged/polar units to form some complex structures observed in experiment, such as diaminoborane (DADB, [(NH3)2BH2^+][BH4]^−). Note that DADB is commonly detected in thermal decomposition experiments of NH3BH3 and has been thought to serve a central role in the decomposition of NH3BH3.

Hydrogen desorption involves many processes, including the formation of native defects, nucleation and growth of new phases, and diffusion of hydrogen to the surface. The computational studies from the defect point of view have mainly focused on the initial stage of hydrogen release. Thus, to understand the full processes and identify the rate-limiting processes in hydrogen release, multiple methods should be used. Molecular dynamics (MD) simulations (ab initio MD or classic MD simulations) and kinetic Monte Carlo (KMC) simulations are powerful tools to identify the diffusivity of constituent species, and have already been used in the study of hydrogen desorption. MD simulation is also a useful method to understand the nucleation and growth of new phases. We expect that a combination of multiple time- and length-scale simulations will be used in the future to understand the (de)hydrogenation processes of storage materials in more detail.

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FUNDING

This work was supported by the National Natural Science Foundation of China (11404409 and 51429101).

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Figure 2. Local structures induced by H-related defects in ammonia borane (NH3BH3). V(HB^3 +) leads to formation of [BH3]^3−, and H^+ results in [BH3]^−. B, N, host H and interstitial H atoms are shown as green, blue, orange and black spheres, respectively.