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Role of charged defects and impurities in kinetics of hydrogen storage materials: A first-principles study

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We identify hydrogen-related point defects as a dominant defect species involved in (de)hydrogenation of sodium alanate, a viable hydrogen storage material. These defects are positively or negatively charged, and hence their formation energies are Fermi-level dependent—an important feature that has not been recognized in past studies. This dependence enables us to explain why small amounts of transition-metal additives drastically alter the kinetics of dehydrogenation. The rate-limiting step for hydrogen release is the creation of *charged* hydrogen-related defects, while transition-metal additives act as electrically active impurities that lower the formation energy of these defects.

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Hydrogen can serve as an energy carrier in a carbon-neutral system of energy production and use,[1,2] but adequate hydrogen storage materials are still lacking in spite of many decades of investigations. In addition to being reversible and meeting stringent wt % and volume criteria, candidate materials must exhibit favorable kinetics for hydrogen uptake and release. Complex hydrides of light elements, such as sodium alanate ($NaAlH_4$), are attractive as storage materials due to their high hydrogen content and demonstrated cycling capability. In 1997, it was discovered that addition of small amounts of transition metals, such as Ti or Zr, drastically enhances the kinetics and allows cycling at temperatures and pressures that are close to optimal.[3] However, the fundamental mechanisms of the (de)hydrogenation process and the effect of transition metals on kinetics in sodium alanate have remained elusive to date.

In this work, we identify hydrogen-related point defects as the species that plays a decisive role in the (de)hydrogenation reactions in $NaAlH_4$. An important feature of these defects is that they are charged, and therefore their formation energy and concentration are strongly affected by the presence of electrically active extrinsic impurities in the material. We show that this provides a consistent explanation for the effect of transition-metal impurities (such as Ti and Zr) on hydrogen kinetics and can reconcile a variety of seemingly conflicting results that have appeared in the literature.[4–14] The hydrogen-related point defects also induce significant rearrangements of the local lattice of the host, thereby providing nucleation sites for reaction [Eq. (1)] shown below.

In $NaAlH_4$, hydrogen release and uptake are accomplished through a sequence of chemical reactions:

$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2, \tag{1}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + \frac{3}{2}H_2. \tag{2}$$

The hydrogen gravimetric capacity for these reactions is 5.6 wt. %. However, in pure $NaAlH_4$, both reactions are slow and proceed only at temperatures too high for practical applications.

Crystal defects are known to play a role in chemical reactions and their presence profoundly affects diffusion and mass transport in materials.[15] In particular, the effect of light- and irradiation-induced defects on the kinetics of $NaAlH_4$ has been established in photolytic decomposition experiments.[16] We have carried out detailed first-principles calculations of the creation of hydrogen-related point defects in $NaAlH_4$ and their diffusion through the material. Our approach is based on density functional theory[17,18] using the generalized gradient approximation[19] and the projector augmented wave method[20] as implemented in the VASP *ab initio* simulation package.[21] The calculations were performed in a supercell containing 96 atoms, with an energy cutoff of 450 eV and a $2\times2\times2$ special *k*-point mesh. Charged defects are treated according to the formalism described in Ref. 22. As discussed there, a compensating background charge needs to be included in order to prevent divergence of the total energy for a charged system. This still leaves a contribution to the total energy due to the electrostatic interactions between the periodic array of charged defects. Makov and Payne[23] proposed to add a correction term (essentially the Madelung energy of a lattice of point charges in a dielectric environment) that would lead to a better estimate of the energy of a single isolated defect. However, this correction has been found to result in an overestimate of the correction term in many cases.[22,24,25] An indiscriminate application of the Makov-Payne correction therefore does not necessarily yield a better approximation of the total energy for an isolated defect. Clearly, more work is needed to better understand these corrections. In the absence of a well justified scheme, we consider it better to refrain from applying any corrections. Note that we do include the so-called "potential alignment" term: the shift in the band positions due to the presence of the defect is taken into account by aligning the average electrostatic potential to the bulk value.[22] Our calculated band gap for $NaAlH_4$ is 4.75 eV. An experimental value of the band gap has not been reported, but density functional theory is known to underestimate the gap; quasiparticle calculations suggest a band gap of 6.9 eV.[26] Migration barriers were calculated using the nudged elastic band method.[27]

In thermodynamic equilibrium, the concentration $c(X)$ of a point defect X at temperature T is given by[22]

$$c(X) = N_{\mathrm{sites}} N_{\mathrm{config}} \exp[-E_f(X)/kT], \tag{3}$$

where N_{sites} is the number of high-symmetry sites in the lattice per unit volume on which the defect can be incorporated and N_{config} is the number of equivalent configurations (per site) in which the defect can be formed. E_f is the formation energy of the defect and is defined as[22]

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(\mathrm{bulk}) - \sum_i n_i \mu_i + q\mu_e. \tag{4}$$

Here, $E_{tot}(X^q)$ and $E_{tot}(\mathrm{bulk})$ denote the total energies of a supercell containing the defect in charge state q and of a supercell containing perfect bulk $NaAlH_4$. Moreover, μ_i is the chemical potential of species i, i.e., the energy of the reservoir with which atomic species i is exchanged, and n_i denotes the number of atoms of species i, which has been added ($n_i > 0$) or removed ($n_i < 0$) to create the defect. μ_e represents the energy of electrons in the charge reservoir, i.e., the electron chemical potential or *Fermi level* (referenced to the top of the valence band). E_f is, in principle, a *free energy*. The effects of vibrational entropy can be significant in $NaAlH_4$ (Ref. 28); however, because E_f reflects energy *differences*, these effects do not affect our conclusions at the temperatures of interest. Vibrational contributions enter in two ways: through zero-point energies and through finite temperature vibrational entropies. A comprehensive calculation of these effects would require an evaluation of the vibrational spectrum for each of the defects that we considered—a huge task which we consider to be beyond the scope of our present work. However, reasonable estimates can be made of both contributions, which show that the effects on the formation energy are, in fact, quite small. It is important to keep in mind that the defect formation energy reflects differences between the system with the defect and the ideal host plus the reservoir. For zero-point energies, important cancellations occur because (for instance) the vibrational modes that are added by placing a hydrogen interstitial in the lattice give similar contributions as the vibrational modes of that hydrogen atom in its reservoir (H_2). We have verified that the net effect on the formation energy is quite small (<0.1 eV). For vibrational entropy, it is actually low-frequency modes that play the most important role, and we expect only modest modifications of such modes due to creation of hydrogen-related defects (since the hydrogen-related modes have high frequencies). Furthermore, since $NaAlH_4$ is stable only below 200 °C, at temperatures of interest, the TS term will not make a significant contribution to the free energy.

Sodium alanate is an ionic compound consisting of sodium cations (Na^+) and covalently bonded anion complexes (AlH_4^-) situated on tetragonal-symmetry sites with an $I4_1/a$ crystallographic space group.[26] Figure 1(a) shows the formation energies for the most relevant intrinsic defects in $NaAlH_4$, namely hydrogen interstitials (H_i) and hydrogen vacancies (V_H) in three possible charge states $(+1, 0, -1)$. In both cases, charged defects are energetically more favorable than neutral states over the entire range of Fermi-level values. Such behavior is characteristic of systems with negative correlation energy U and usually occurs in conjunction with large lattice relaxations,[29] as discussed below.

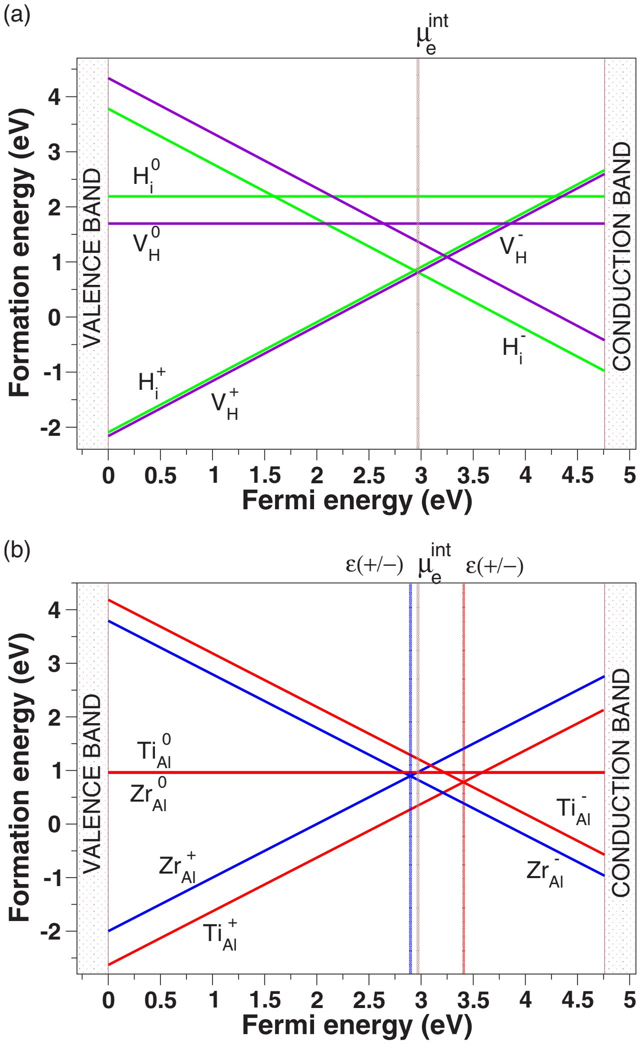

FIG. 1. (Color online) Calculated formation energies of relevant defects and impurities in $NaAlH_4$ as a function of Fermi level. The vertical lines denote the Fermi-level position determined by charge neutrality. (a) Hydrogen-related defects. Equilibrium with H_2 molecules at $T=0$ is assumed. (b) Ti-related (red) and Zr-related (blue) defects. For Ti and Zr, the chemical potentials were fixed to the energy of the bulk metals and Al-rich conditions were assumed.

The concentrations of charged defects are not independent but coupled by the condition of charge neutrality,

$$\sum_j q_j c(X_j^{q_j}) - n + p = 0. \tag{5}$$

The first term is a sum over all defects $X_j^{q_j}$ in charge state q_j, n is the concentration of electrons in the conduction band, and p is the concentration of holes in the valence band. In an insulator such as $NaAlH_4$, the concentrations of free carriers n and p are very small, and therefore charge neutrality is accomplished by incorporation of defects with opposite charges. The relevant point defects and impurities introduce defect levels that are deep in the band gap, causing the resulting Fermi-level positions to be far from the band edges and justifying the neglect of n and p in Eq. (5). The defects with the lowest formation energy have the highest concentrations and dominate in Eq. (5). Figure 1(a) therefore indicates that, in the absence of extrinsic impurities, the Fermi level will have the value $\mu_e^{int}=2.97$ eV where the formation energies of V_H^+ and H_i^- are equal.

We now turn our attention to the incorporation of extrinsic impurities such as Ti or Zr, for which we have explored both substitutional and interstitial configurations. The lowest formation energies were obtained for the impurity substituting on an Al site; the preference over the Na site is consistent with the chemical similarity of these transition-metal impurities with Al and also with recent x-ray diffraction results.[9] Figure 1(b) shows that Ti_{Al} also acts as a "negative-U" center. The Fermi-level position where positive and negative charge states have equal formation energies determines the transition level $\varepsilon(+/-)$.[22] If Ti_{Al} is present in concentrations exceeding those of other charged defects, the Fermi level will be pinned at $\mu_e=\varepsilon(+/-)=3.41$ eV. This is true irrespective of whether Ti_{Al} is incorporated under equilibrium or nonequilibrium conditions (including processes such as ball milling[12]), since it is driven by equilibration of electronic states for Ti at a single site.

Incorporation of an electrically active defect such as Ti therefore has the important effect of shifting the Fermi level from its value in intrinsic material, in this case by an amount $\Delta\mu_e=\varepsilon(+/-)-\mu_e^{int}=+0.44$ eV. This shift changes the formation energy of the predominant hydrogen-related point defect (H_i^-) by $\Delta E_f=-0.44$ eV. This decrease in E_f causes an increase in the concentration of the defect, resulting in an increase in self-diffusion. The kinetics of hydrogen-related point defects is intimately tied to the decomposition reaction [Eq. (1)], and a lowering of E_f allows achieving a given concentration of defects at a lower temperature; experimentally, Ti-induced decreases of the decomposition temperature $\Delta T\approx 60$ °C (Ref. 3) and $\Delta T\approx 100$ °C (Ref. 30) have been reported. Using Eq. (3), we also find that the decrease $\Delta E_f=-0.44$ eV at a given temperature results in an increase of the defect concentration by 6 orders of magnitude. The defect concentrations can rise to about 10^{17} cm^{-3}, which (in combination with the low migration barriers discussed below) is more than adequate to cause copious amounts of self-diffusion. At the same time, such concentrations are small enough to fulfill the condition that the hydrogen-related defects have no effect on the Fermi-level position in the presence of an extrinsic impurity. Indeed, Ti_{Al} concentrations well exceeding 10^{17} cm^{-3} should be easily attainable in doped material, given that typically, several mol % of Ti are added (corresponding to concentrations above 10^{20} cm^{-3}). In fact, our findings emphasize that only a small fraction of this added Ti is needed to achieve the desired effect.

Experimentally, several Ti-related species have been detected in $NaAlH_4$.[7,10,13,14,31,32] However, those experiments that directly investigated the correlation between observed species and the enhancement of kinetics found that only a minute fraction of the total Ti present produces the observed enhancements.[8,33,34] For instance, the electron paramagnetic resonance studies of Ref. 8 demonstrated that the majority of the Ti is inactive. Ti-Al alloy formation has also been reported; such alloys have been proposed as a surface catalyst,[6,7,13] but they were also found to be an inactive species.[8] Our results strongly suggest that the presence of these alloys is not required in order to achieve a significant enhancement in the kinetics of the alanate.[8] This is good news from the point of view of technological applications since adding large amounts of Ti adversely affects the hydrogen weight capacity. Extended defects (e.g., grain boundaries) have frequently been mentioned as an explanation for fast diffusion. Such effects may indeed be present in $NaAlH_4$. However, our results demonstrate that the presence of such extended defects is not required for fast diffusion of hydrogen-related defects to be possible.

Since the kinetics of hydrogen-related point defects is intimately tied to the decomposition reaction [Eq. (1)], we expect that our calculated decrease in the defect formation energy ΔE_f would be reflected in the experimentally observed change in activation energy ΔQ for Ti-doped alanate compared to that for pure alanate. $\Delta E_f=0.44$ eV corresponds to 42 kJ/mol, in very good agreement with reported values (~40 kJ/mol).[33] The observed lowering was independent of the amount of added Ti, which is consistent with our statement that as long as the Ti_{Al} concentration exceeds the concentration of hydrogen-related defects, the Fermi level will be pinned at the $\varepsilon(+/-)$ transition level, irrespective of the Ti concentration.

The results presented in Fig. 1(b) demonstrate that a similar mechanism applies in the case of Zr doping. Zr also exhibits negative-U behavior, and the Fermi level is pinned at $\varepsilon(+/-)=2.90$ eV. The Zr-induced shift in the Fermi level ($\Delta\mu_e=-0.07$ eV) and hence in E_f is much smaller than in the case of Ti, resulting in a much smaller impact on reaction kinetics. An experimental comparison of Ti- and Zr-doped alanate indeed suggested a change in the activation enthalpy between Ti- and Zr-doped samples of 30 kJ/mol.[35] Combined with the result for Ti cited above, this implies an activation energy lowering of only ~10 kJ/mol over the value of undoped alanate, consistent with our estimated value of 0.07 eV or ~7 kJ/mol.

Figure 2 illustrates the remarkable changes in lattice geometry induced by the presence of hydrogen-related defects or Ti. All of the defects induce significant modifications of one or more surrounding AlH_4^- complexes, which in pure alanate exhibit close to tetrahedral geometry. Changes in the coordination number of Al and H atoms as well as in the symmetry of the resulting Al-H complexes are observed. Hydrogen vacancies and interstitials induce the formation of threefold coordinated, almost planar AlH_3 complexes with slightly distorted C_{3v} symmetry. A fivefold coordinated Al-H complex is evident in the presence of H_i^- and Ti_{Al}; it exhibits distorted C_s symmetry and resembles an AlH_6 complex with one H missing. The presence of Ti also induces an onset of octahedral coordination similar to that of AlH_6^{3-} in the Na_3AlH_6 phase, although the H atoms are shared with other Al atoms. All of these structural rearrangements suggest that the defects studied here also play a role in the nucleation of other phases during the solid-state reaction [Eq. (1)]. In particular, Al-H complexes with higher than fourfold coordina-

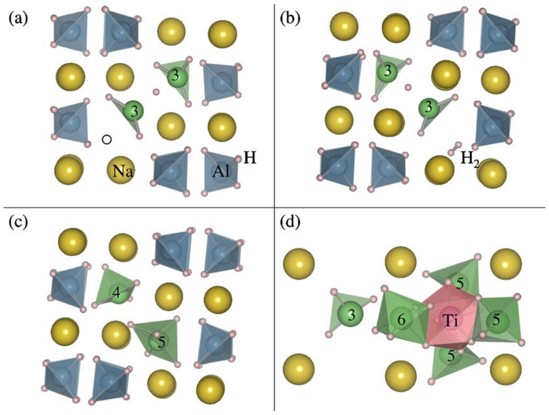

FIG. 2. (Color online) Lattice relaxations induced by hydrogen-related defects and impurities in $NaAlH_4$. The numbers indicate coordination of (distorted) AlH_x complexes (in green). Background undistorted tetrahedral complexes were removed for clarity. (a) Positively charged hydrogen vacancy V_H^+. Removal of a hydrogen atom (indicated by the open circle) from an AlH_4 complex leads to the formation of a planar AlH_3 complex; the Al atom in this complex moves toward the neighboring AlH_4, partially attracting one of its H atoms and resulting in the formation of a second AlH_3 complex with planar geometry. Structural rearrangements in the case of V_H^- (not shown here) are much smaller. (b) The positively charged hydrogen interstitial (H_i^+) decays into a H_2 molecule and a positively charged hydrogen vacancy. (c) Negatively charged hydrogen interstitial H_i^-. One Al atom becomes fivefold coordinated, and a distorted AlH_4 is evident. (d) Substitutional Ti on an Al site (Ti_{Al}^+) causes large local lattice rearrangements involving the surrounding AlH_4 complexes.

tion can serve as nucleation sites for the Na_3AlH_6 phase.

Last but not least, we address the mobility of the defects. For H_i^-, we calculated a migration barrier (i.e., the energy difference between the saddle point and the ground state) $E_m=0.22$ eV. For V_H^+, the path was calculated by moving a hydrogen atom from a nearby AlH_4 complex into the vacancy, resulting in $E_m=0.26$ eV. The diffusion coefficient is given by $D=D_0\exp(-E_m/kT)$, with $D_0\approx 0.07$ cm^2/s based on the vibrational frequency and the jump length. Once formed, these defects are therefore highly mobile and can easily traverse macroscopic distances at temperatures below room temperature. These results agree well with the observation of highly mobile hydrogen-related defects in Ref. 36. The low value of the migration barriers indicates that the formation energy E_f of the hydrogen-related defects is the dominant term in the activation energy for self-diffusion, and that defect migration is not a rate-limiting step. These low barriers also confirm that the formation of hydrogen-related point defects can be treated as an equilibrium process, an assumption that underlies Eq. (3).

We predict that the presence of charged hydrogen-related defects should lead to observable ionic conductivity in $NaAlH_4$. The conductivity is given by $\sigma=e^2cD/kT$, where e is the electron charge, c the concentration [see Eq. (3)], and D the diffusion coefficient as defined above. The predicted conductivity is low in undoped alanate at 100 °C [$\sigma \approx 10^{-11}$ $(\Omega\ \mathrm{cm})^{-1}$] but increases to $\sigma\approx 10^{-5}$ $(\Omega\ \mathrm{cm})^{-1}$ in Ti-doped material. Experimental measurements are called for.

In summary, we have described a mechanism for (de)hydrogenation of sodium alanate that highlights the role of charged hydrogen-related point defects and electrically active impurities. Our comprehensive first-principles calculations quantitatively confirm that the proposed mechanisms play a crucial role and provide testable predictions as well as specific results that compare favorably with existing experiments. While our detailed results focus on sodium alanate, the concepts are general and may apply to other hydrogen storage materials. The ideas outlined here suggest improved preparation methods for complex hydrides through enhanced control of the addition of small concentrations of impurities. More generally, the awareness of the role played by charged defects and the importance of Fermi-level control should aid in design of a wider range of hydrogen storage materials.

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