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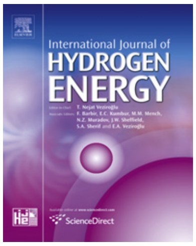

Technical Communication

AlH_3-mediated mechanism in hydriding/dehydriding of $NaAlH_4$

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ABSTRACT

By theoretical investigation, we found that the balanced Fermi level in $NaAlH_4$ is pinned by the vacancy pair of its ionic components (V_{Na}^- and $V_{AlH_4}^+$), which significantly affects the formation enthalpies of other possible charged defects. V_{Na}^- and $V_{AlH_4}^+$ easily form $V_{Na-AlH_4}^0$ vacancy complex on surface but not in bulk. This helps the diffusion of V_{Na}^- and $V_{AlH_4}^+$, but will not induce the decomposition of $NaAlH_4$ directly. In fact, we found that $V_{AlH_3}^0$ plays a critical role in the decomposition of $NaAlH_4$ and an AlH_3-mediated mechanism for the hydriding/dehydriding of $NaAlH_4$ is suggested.

$NaAlH_4$ is regarded as one of the best prototype materials for the studies on complex hydrides as hydrogen storage materials. Na_3AlH_6 and NaH are experimentally identified during the decomposition of $NaAlH_4$ [1]. Although the detail of the decomposition of $NaAlH_4$ is not yet fully understood [2], the putative (de)hydrogenation pathway is accepted as follows [1]:

$$NaAlH_4 \leftrightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \quad (1)$$

$$Na_3AlH_6 \leftrightarrow 3NaH + Al + \frac{3}{2}H_2 \quad (2)$$

Later, Gross et al. [3] found through in-situ XRD experiments that there exist a new phase undoubtedly before the formation of Na_3AlH_6, and they suggested that there should be several micro-reaction processes involved in the above two macro-apparent reactions. Furthermore, a series of micro-reaction steps of $LiAlH_4$ was reported by Kang et al. [4], and there are other research works [2,5] which supported the viewpoint of Gross et al.

It is well known that many Ti-contained materials are effective catalyst for the (de)hydrogenation of $NaAlH_4$ [1,6,7] while the detailed catalyzing mechanism of Ti is still unclear. Understanding the micro-hydriding/dehydriding mechanism of $NaAlH_4$ is a prerequisite to the role of Ti on $NaAlH_4$, as well as the design of high performance catalysts of $NaAlH_4$, since the catalytic effect is generally achieved by reducing the kinetic barrier of certain micro-reaction processes. It is realized that the first dehydriding step in micro-dehydriding processes of $NaAlH_4$ is the formation of

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some H-contained vacancies, a focus of this work, though the micro-hydriding/dehydriding processes of $NaAlH_4$ is still lack adequate study. Note that earlier works [8,9] on intrinsic defects of $NaAlH_4$ did not aim at the micro-reaction of $NaAlH_4$ by comparing all the intrinsic defects of $NaAlH_4$ systematically. Besides, their investigations are not directly related to the practical hydriding/dehydriding condition [10] of $NaAlH_4$.

$NaAlH_4$ crystal is a wide band gap ionic crystal, where its intrinsic defects are often charged. The formation enthalpies of charge defects depend on the balanced Fermi level [11] which involves all the intrinsic defects. As a result, all the defects need to be considered systematically, although our target is to find out a micro-dehydriding mechanism by comparing the formation enthalpies of H-contained vacancies in $NaAlH_4$. In this work, we study intrinsic defects of $NaAlH_4$ as many as we can. We have considered single vacancies, interstitial defects, antisite defects, and complex defects. The surface effect is also discussed for these defects by comparing their formation enthalpies to those in bulk. All the combination of the single defects and their nearest neighbor (NN) defects for complex defects are taken into account. The surface we consider here is the (001) surface, which has the lowest surface energy in $NaAlH_4$.

We have performed DFT plane-wave calculations for a $3 \times 3 \times 1$ supercell and a 7 layers 2×2 (001) slab of $NaAlH_4$ with the VASP code [12,13]. A vacuum space of 15 Å along the z direction is employed to simulate the surface. The Al and Na ions in the 3 bottom layers of the slab are fixed, while all the H ions are relaxed. Brillouin zone is generated by the Monkhorst–Pack scheme with $3 \times 3 \times 3$ for the supercell and $5 \times 5 \times 1$ for the slab. The cut-off energy for plane waves is 500 eV. Defect formation enthalpies in bulk and surface were calculated with Eq. (1) [14].

$$H_f^{D,q}(E_F, \mu) = E^{D,q} - E(\text{bulk/slab}) + \sum_i n_i \mu_i + q[E_V(\text{bulk/slab}) + E_F] \tag{3}$$

Here, $E^{D,q}/E$ are total energy with/without defect, respectively; E_v(bulk/slab) is the energy at the valence band maximum (VBM) in bulk/slab without defects. Our calculated value, 4.75 eV, is adopted here for the band gap of $NaAlH_4$, since we cannot find any experimental value. Here the image charge correction [15] (typically within 200 meV) is not employed, which is not expected to affect our conclusion since we are not dealing with the shallow levels of semiconductors.

The defect formation enthalpy is influenced by the chemical environment which can be characterized by chemical potentials of related atoms, *i.e.* μ_i in Eq. (3). The chemical environment at the hydriding/dehydriding critical point of $NaAlH_4$ [10] is adopted for the intrinsic defect study, which is corresponding to the H-poorest condition.

The intrinsic defects in bulk of $NaAlH_4$ are studied firstly in consideration of their relative simplicity in structure due to higher defect symmetry in bulk with respect to surface. Calculated formation enthalpies of intrinsic defects in bulk of $NaAlH_4$ as a function of Fermi level are shown in Fig. 1. For a clear view, only some easy-to-form defects and some representative defects with high formation enthalpy are shown.

From Fig. 1, it is clear that the balanced Fermi level of $NaAlH_4$ crystal is pinned by V_{Na}^- and $V_{AlH_4}^+$ around the value of 3.30 eV above the VBM of bulk $NaAlH_4$, which is close to the middle of the band gap. All the single vacancies and interstitial defects are in charged state at the balanced Fermi level.

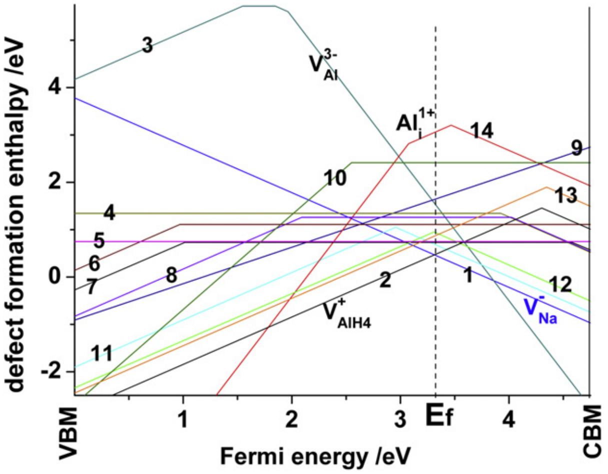

Fig 1 – Calculated defect formation enthalpies of defects in bulk of $NaAlH_4$ at the hydriding/dehydriding critical point as a function of Fermi level. (1) V_{Na}, (2) V_{AlH4}, (3) V_{Al}, (4) V_{NaH}, (5) $V_{Na-AlH4}$; (6) V_{AlH}; (7) V_{AlH3}; (8) V_{H-H}; (9) Na_i; (10) Al_{Na}; (11) H_i; (12) V_H; (13) V_{AlH2}; and (14) Al_i. The dashed line indicates the pinned Fermi level under the charge neutral condition.

In the whole band gap, Na vacancy exists in the state of V_{Na}^-, and the interstitial Na defect shows 1+ charge state, clearly as a result of strong ionicity of Na. There are mixed covalent and ionic bonds for Al and H [16,17]. Consequently, they are at different charge state as the Fermi level shifts in the band gap. Both the transition levels [14,15] of V_H^+ and V_H^- are around the equilibrium Fermi level. Furthermore, the formation enthalpy of interstitial Na, Al, or H defect is higher than that of its corresponding vacancy, especially for Al and Na. It is clear that Al-contained defects mainly exist in the form of complex defect due to the high formation enthalpies of its interstitial and vacancy single defects. The antisite defect Al_{Na}^0 can be regarded as Al_i^+ in the vacancy of V_{Na}^-. Although the formation enthalpy of V_{Na}^- is the lowest among all the intrinsic defects, Al_{Na}^0 is hard to form with its high formation enthalpy of 2.41 eV. It is expected that other antisite defects are difficult to exist too.

The charge state of complex defects is related to the situation of their components. The H–H complex vacancy favors neutral state as V_H^+ and V_H^- attracts each other by Coulomb interaction, i.e. $V_H^+ + V_H^- \leftrightarrow V_{H-H}^0$. Meanwhile, we have $V_H^+ + V_{Na}^- \leftrightarrow V_{NaH}^0$, $V_{AlH_4}^+ + V_{Na}^- \leftrightarrow V_{Na-AlH_4}^0$ and $V_{Al}^{3+} + 3V_H^- \leftrightarrow V_{AlH_3}^0$. We also have $V_{AlH_3}^0 \leftrightarrow V_{AlH}^0 + V_{H-H}^0$ and $V_{AlH_4}^+ \leftrightarrow V_{H-H}^0 + V_{AlH_2}^+$ for AlH and AlH_2 vacancies.

It is shown in Fig. 1 that there are seven intrinsic defects with formation enthalpy lower than 1.0 eV in bulk $NaAlH_4$, and their formation enthalpies arranged from low to high in the following sequence: $V_{Na}^-/V_{AlH_4}^+ < H_i^- < V_{AlH_3}^0 < V_{Na-AlH_4}^0 < V_{AlH_2}^+ < V_H^+/V_H^-$.

Regarding the intrinsic defects on the surface of $NaAlH_4$, its most stable surface (001), is studied here. While (001) surface is expected to dominate the rehydrogenation process due to its high stability, the formation energy of H-contained vacancies on (001) surface provides the upper limit for the dehydrogenation process in various surfaces. We only consider the corresponding 7 easy-to-form defects here, because other defect concentrations are expected to be low as the situation in bulk. The formation enthalpies of studied surface defects are listed in Table 1, as well as those for the bulk defects.

We find that the local structure and charge state of the corresponding defects on surface are similar to that in bulk. Both on surface and in bulk, the AlH_3 and $NaAlH_4$ vacancy complexes are neutral, and the AlH_4 and AlH_2 vacancy complexes exist in 1+ charge state, while the interstitial H and Na vacancy present in 1− charge state. The transition level of V_H^- and V_H^0 on (001) surface is also around the equilibrium Fermi level as that of V_H^- and V_H^+ in bulk.

According to Table 1, the most favorable intrinsic defect on the (001) surface is $V^0_{Na-AlH_4}$. The calculated binding energy for V_{Na}^- and $V^+_{AlH_4}$ in bulk is only 0.20 eV, indicating that V_{Na}^- and $V^+_{AlH_4}$ do not often couple to each other in bulk. On the surface, V_{Na}^- and $V^+_{AlH_4}$ mostly appears as a coupled complex since the calculated binding energy of V_{Na}^- and $V^+_{AlH_4}$ on surface is as great as 1.22 eV. Hereby, $V^0_{Na-AlH_4}$ on surface is a kind of paired Schottky defect, which is consistent with the general phenomena of defects in ionic crystal. Here, we suggest a mechanism for the formation process of $V^0_{Na-AlH_4}$ on $NaAlH_4$ surface. First, AlH_4^- and its nearest neighbor Na^+ get away together as a complex from surface and move to a new lattice point at boundary, leaving $V^0_{Na-AlH_4}$ at the original surface. Then, AlH_4^- and Na^+ ions at inner layer fill in the vacancy site of $V^0_{Na-AlH_4}$. Analogously, AlH_4^- and Na^+ at the inner lattice point of bulk move outwards to form a new surface of $NaAlH_4$ iteratively. The relative weak coupling between V_{Na}^- and $V^+_{AlH_4}$ in bulk can actually speed up their migration process. It should be pointed out that during the formation process of $V^0_{Na-AlH_4}$, it does not induce direct decomposition of $NaAlH_4$ as Na^+ and AlH_4^- are just moved from the original surface to a new one.

From our calculated results H_i is an easy-to-form defect with a formation enthalpy of 0.69 eV. Therefore, the interstitial site can be considered as a trap of H ion which hinders migration of H [18]. Besides, we expect that H_i can play another role. If an AlH_4 group gains energy from environment, AlH_3–H separation [8,19] probably takes place by the trap of nearby H_i. It should also be pointed out here that the Frank defect H_i does not induce the decomposition of $NaAlH_4$.

Table 1 – The formation enthalpies of typical easy-to-form intrinsic defects in bulk and on (001) surface of $NaAlH_4$ under the critical point (unit: eV).

Bulk		(001) Surface	
Defect	H_f	Defect	H_f
V_H^+/V_H^-	0.93	V_H^-/V_H^0	1.54
V_{Na}^-	0.47	V_{Na}^-	0.72
H_i^-	0.69	H_i^-	1.49
$V^0_{AlH_3}$	0.73	$V^0_{AlH_3}$	0.64
$V^+_{AlH_4}$	0.47	$V^+_{AlH_4}$	0.97
$V^0_{Na-AlH_4}$	0.74	$V^0_{Na-AlH_4}$	0.47

In bulk, the formation enthalpy of $V^0_{AlH_3}$ is just a bit higher than that of H_i,V_{Na}^-, or $V^+_{AlH_4}$. Particularly, $V^0_{AlH_3}$ is the second easy-to-form defect on the surface. In our calculated results, the local structure of $V^0_{AlH_3}$ in bulk and on surface of $NaAlH_4$ is similar to each other, which is a "AlH_5 complex + vacancy" structure, in line with the result of Gunaydin et al. [8]. Besides, the AlH_5 complex is a precursor of AlH_6 [8], the anion group of Na_3AlH_6. According to our earlier results [10], the AlH_3 crystal is stable only in the region of Al-rich and H-rich, which is far from the hydriding/dehydriding critical point of $NaAlH_4$. Obviously, the stability of AlH_3 molecules is lower than that of the AlH_3 crystal. Therefore, the escaped AlH_3 molecules from $NaAlH_4$ during the formation of $V^0_{AlH_3}$ would finally decompose into Al and H_2 at the critical point. It is easy to know that the formation process of $V^0_{AlH_3}$ (micro) is consistent with the well-known first step decomposition equation of $NaAlH_4$ (macro) [1]. As a precursor of Na_3AlH_6, AlH_5 may be generated within the matrix during the formation of $V^0_{AlH_3}$ at the critical point, coupled with the escape of AlH_3, a precursor of H_2. Therefore, $V^0_{AlH_3}$ may play a critical role in the initial stage of the decomposition of $NaAlH_4$. Particularly, the formation energy of $V^0_{AlH_3}$ is the lowest among those H-contained vacancies that possibly induces the decomposition of $NaAlH_4$. In addition, we know that hydrogen releases rightly at the hydriding/dehydriding critical point [10], where the formation enthalpy of $V^0_{AlH_3}$ reaches the minimum value. That is to say, the micro- and macro-processes are consistent with each other from the chemical environment aspect.

When an AlH_3 molecule escapes from the surface and decomposes to Al and H_2. The Al atom from the decomposed AlH_3 should grow on surface, which induces the formation of $NaAlH_4$/Al interface [20]. Meanwhile, the $NaAlH_4$/Al interface is an Al-richest and H-poorest environment [10], which is corresponding to the chemical environment of the hydriding/dehydriding critical point and facilitating the formation of $V^0_{AlH_3}$. The concentration of $V^0_{AlH_3}$ on surface is higher than that in bulk of $NaAlH_4$ and the migration ability of $V^0_{AlH_3}$ is rather well [8]. Therefore, $V^0_{AlH_3}$ moves into bulk easily once it forms at surface or $NaAlH_4$/Al interface. It should be pointed out that the migration of $V^0_{AlH_3}$ from surface into bulk can be regarded as a process of AlH_3 moving from bulk to surface.

Based on the above discussions, we put forward an AlH_3-mediated mechanism for the dehydrogenation process of $NaAlH_4$. It is suggested that during the dehydriding of $NaAlH_4$ there is an intermediate state of metastable AlH_3 molecule, whose decomposition actually releases hydrogen, instead of the decomposition of the matrix directly. This mechanism involves several critical steps (*c.f.* Fig. 2):

1. At first, AlH_3–H separation occurs in AlH_4 groups at surface.
2. Then, the AlH_3 escapes from the lattice point of surface and it is probably adsorbed at the matrix surface, *i.e.*, $V^0_{AlH_3}$ is formed at the surface.
3. Next step is the migration and decomposition of AlH_3, followed by the growth of Al cluster and the formation of $NaAlH_4$/Al interface.
4. $V^0_{AlH_3}$ at the surface or $NaAlH_4$/Al interface migrates into bulk (or AlH_3 move from bulk to surface/interface).

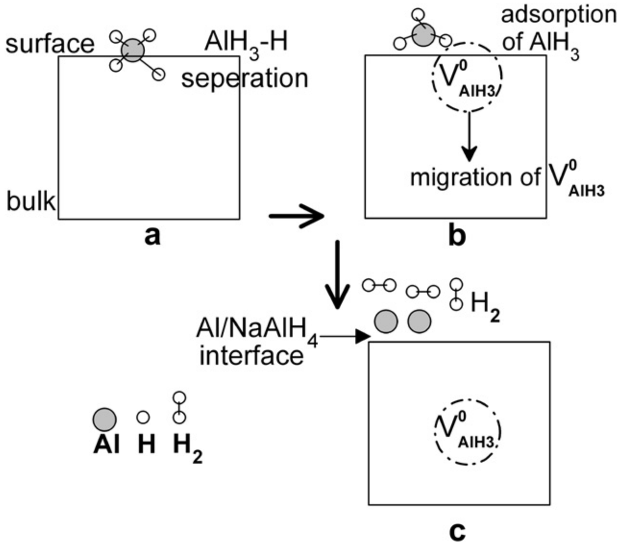

Fig. 2 – Sketch map of the AlH_3-mediated mechanism. (a) AlH_3–H separation of AlH_4 group; (001) surface of $NaAlH_4$; (b) formation of $V^0_{AlH_3}$ and adsorption of AlH_3 molecular; (c) decomposition of AlH_3, migration of $V^0_{AlH_3}$, nuclear and growth of Al and the formation of Al/$NaAlH_4$ interface.

Steps 1–4 are reiterated under certain thermodynamic conditions, and thus $NaAlH_4$ is decomposed.

Regarding the rehydriding of $NaAlH_4$, it is generally harder to take place than the dehydriding under the normal experimental condition. This could be due to the intrinsic metastable property of AlH_3 molecules, which is reflected by the fact that AlH_3 molecules are seldom detected in experiments. Meanwhile, it was reported that the rehydriding becomes much easier through AlH_3 directly [21,22]. It is clear from the above observation that the rehydriding of $NaAlH_4$ will be significantly enhanced if AlH_3 molecules are stabilized. Therefore, the AlH_3 mechanism is consistent with the experimentally observed rehydrogenation process of $NaAlH_4$ too. The rehydriding could be improved by increasing the stability of intermediate AlH_3, which also brings a better chemical equilibrium between hydriding and dehydriding.

The suggested AlH_3 mechanism above is also in line with the catalyst effect of Ti to $NaAlH_4$. For example, Chaudhuri et al. [23] found that Ti can promote the decomposition of H_2 and the bonding between H and Al during hydriding, and they point out that the formation of alane species are the key to the synthesis of the next products in the rehydrogenation reaction. In addition, Ti can reduce the formation enthalpy of $V^0_{AlH_3}$ [8] in dehydriding. The direct experimental evidence for the AlH_3 mechanism is that Fu et al. [24] detected $(AlH_3)_n$ molecules during the hydriding/dehydriding of $NaAlH_4$. While it is the only experiment that detected AlH_3 molecules up to now, other experimental techniques, such as femto-second pulsed lasers, are suggested to provide further evidence for the AlH_3 mechanism. Finally, the suggested AlH_3 mechanism implies several key factors to enhance hydriding/dehydriding performance of $NaAlH_4$, *i.e.*, increasing the stability of absorbed AlH_3, enhancing the AlH_3–H separation [8,19], decreasing the migration barrier of AlH_3 and/or $V^0_{AlH_3}$, and improving the growth process of Al.

In summary, a metastable AlH_3 mechanism as a micro-step for dehydrogenation and hydrogenation of $NaAlH_4$ is suggested from the thermodynamic of defect aspects, which is supported by experimental observations in the literature.

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