
First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides

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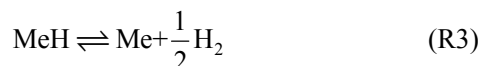
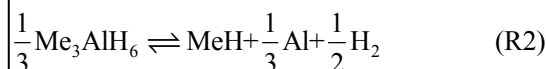
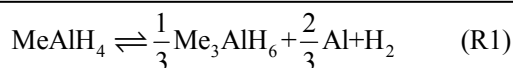
Project Scope

Our goal is to develop a multiscale approach to model desorption and adsorption of hydrogen in complex metal hydrides. In this initial stage of the project, we started by using density-functional-theory quantum chemical calculations to study the structure of complex metal hydrides and the interactions of hydrogen with the metal atoms in these hydrides. We analyzed the crystal structure of LiAlH_4 , NaAlH_4 , KAlH_4 as well as LiBH_4 and determined the stability of different crystal surfaces of these hydrides. We further studied the thermodynamics of hydrogen desorption from the surfaces by creating hydrogen vacancies on the surfaces. We identified a precursor state for the formation of TiAl_3 complex in Ti-doped NaAlH_4 and explored its possible roles in reversible hydrogen desorption/adsorption.

Recent Progress

(a) *Density functional theory analysis of intrinsic surface properties of complex metal hydride.*¹

Effective on-board hydrogen storage systems are required to have appropriate thermodynamics, fast kinetics, and high storage capacities and densities. Among various possible hydrogen storage technologies, solid-state method offers perhaps the best opportunities for meeting the requirements of on-board application. In particular, alanate-based complex metal hydrides show great promises for meeting the requirements. The alanates release hydrogen through a series of decomposition / recombination reactions,



where Me represents Li, Na, or K. For the most widely studied NaAlH_4 , the first two combined reactions give a theoretical reversible hydrogen-storage capacity of 5.6 wt% at the temperatures lower than 250°C out of a total content of 7.5 wt%. For LiAlH_4 and KAlH_4 , the first two steps would produce a theoretical reversible hydrogen capacity

of 7.9% and 4.3%, respectively. The mechanism involves a series of complex steps of heterogeneous reactions and phase transitions. This mechanism is significantly different from the hydrogen storage mechanism in the conventional metal hydrides in which hydrogen atoms are the only mobile species. In this project, low-index surfaces, (001), (010), (100), and (101), have been created by constructing slabs from the relaxed bulk MeAlH_4 structures. All the surfaces have been built without breaking Al–H bond of the AlH_4^- unit. The thickness of the slab in each case is about 12 Å and the vacuum region separating the slab from its periodic images is larger than 15 Å. The surface energy, in J/m^2 , is calculated by the following formula:

$$\sigma_{surf} = \frac{1}{2A}(E_{stoi} - nE_{bulk}) \quad (1)$$

where A is the area of the surface unit cell, E_{stoi} and E_{bulk} are the total energy of a stoichiometric slab and the total energy of one formula MeAlH_4 in the bulk, respectively. The number of MeAlH_4 formula in the slab is represented by n. The results are summarized the Table 1.

In order for alkali alanate to release hydrogen, the Al – H bonds in the compound have to be broken. Therefore, the properties of the defected surfaces formed by removing H atoms from the surfaces have been studied. In general, the formation energy of H vacancies is defined as,

$$\Delta E_{vac} = \frac{1}{2n}(E_{vac} - E_{stoi} + nE_{H_2}) \quad (2)$$

where E_{vac} is the total energy of the slab with hydrogen vacancy and is a measure of hydrogen desorption energy from the surface the these alanates. The formation energy was averaged over the vacancies in the same unit cell and the factor of 2 accounts for the two-sided slab. E_{H_2} is the total energy

of a free H_2 molecule calculated in a large box. The calculated energy costs to create the defects are summarized in Table 2.

The energy cost to create a single H vacancy represents the low-limit of the activation energy for hydrogen desorption from an ideal surface. By comparing with our results from an earlier study of $LiBH_4$ study,² we found that this energy correlates strongly with the intrinsic H-M bond energy, i.e. H-B \gg H-Al (340 vs 284 kJ/mol for gas phase molecules), in the complex hydrides but correlates weakly with the alkali ions.

(b) A precursor state for formation of $TiAl_3$ complex in reversible hydrogen desorption/adsorption from Ti-doped $NaAlH_4$.³

Extensive experimental studies of Ti-doped $NaAlH_4$ have led to considerable improvement in the kinetics and cycling performance at the conditions that are relevant to the practical operation of a proton exchange membrane fuel cell. Despite of the progresses, the mechanism and process that the $NaAlH_4$ system is catalyzed by a small amount of Ti is not well understood. In general, the heterogeneous reactions such as hydrogen release and uptake in Ti-doped $NaAlH_4$ are complex and difficult to study. We first established the preferred site of Ti in Ti-doped $NaAlH_4(001)$ and focused on three types of sites: (1) Ti is adsorbed on the surface and linked with two neighboring AlH_4^- hydrides; (2) Ti replaces Na^+ in the lattice, making Na^+ displace upward or downward; (3) Ti is located in the interstitial sites and connected with three hydrides. Our results clearly show that Ti in the interstitial sites, with a binding energy of 4.182 eV, is most stable among all these structures.

In the relaxed structures, the Ti atom occupies the interstitial space among three hydrides and is bound directly with three Al atoms, as shown in Figure 1(a). This interstitial space is accessible directly from the surface. The stronger affinity of Ti toward H than Al makes Ti strip hydrogen from Al. We refer it to as $TiAl_3H_x$ for simplicity but note that Ti-H bonds are formed

Table 1. DFT-GGA surface energy of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$.

	(001)	(010)	(100)	(101)
$LiAlH_4$	0.205	0.176	0.160	0.192
$NaAlH_4$	0.146	0.327	0.327	0.246
$KAlH_4$	0.104	0.132	0.157	/

Table 2. Hydrogen desorption energy (eV) from the surfaces of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$.

	(001)	(010)	(100)	(101)
$LiAlH_4$	1.324	1.472	1.293	1.319
$NaAlH_4$	1.390	1.227	1.308	1.299
$KAlH_4$	1.349	1.369	1.338	/

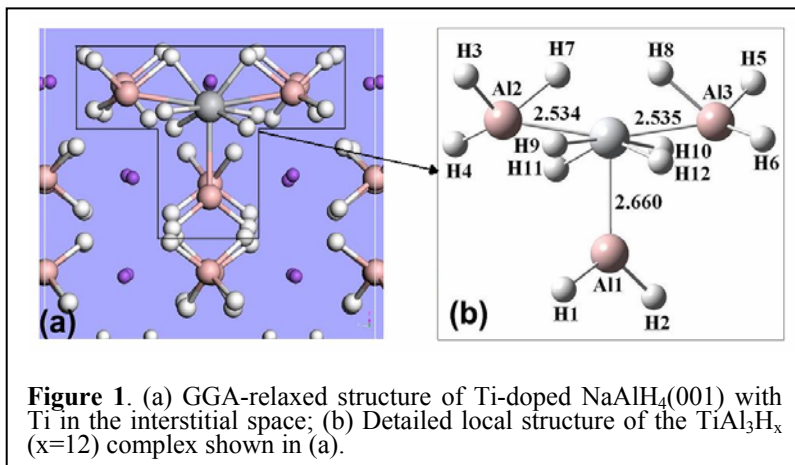


Figure 1. (a) GGA-relaxed structure of Ti-doped $NaAlH_4(001)$ with Ti in the interstitial space; (b) Detailed local structure of the $TiAl_3H_x$ ($x=12$) complex shown in (a).

in the complex structure. The detailed local structure of a TiAl_3H_x complex with $x=12$ is shown in Figure 1(b). We then studied the energetics of hydrogen desorption on the basis of the most stable structure determined above. Herein, we define desorption energy as the total energy difference between the Ti-doped stoichiometric slab and the sum of the slab with hydrogen atoms removed and hydrogen molecules. Hydrogen desorption energies with hydrogen atoms from different positions of the complex structure shown in figure 1b were summarized in Table 3. For comparison, we also calculated the energy cost to desorb a pair of hydrogen atoms from the same AlH_4^- unit on the (001) surface of pure NaAlH_4 . This energy is 1.383 eV per H_2 molecules. Clearly, to desorb hydrogen from the Ti-containing complex is energetically favorable over the direct desorption from pure NaAlH_4 . Furthermore, the energy required to desorb the first 4 hydrogen molecules from the complex is ~ 3.3 eV, indicating that the heat released from doping the Ti atoms would be sufficient to maintain the energy balance.

Table 3. DFT-GGA hydrogen desorption energies with different combinations of hydrogen atoms in the local structure TiAl_3H_x ($x=12$) shown in Figure 1b.

Combination of hydrogen atoms	Desorption energy (eV/ H_2 molecule)
H1,H2	0.515
H3,H4,H5,H6	0.921
H9,H10	0.934
H11,H12	1.265
H7,H8	2.067

The complex TiAl_3H_x structure may play important roles in the reversible hydrogen release/uptake in Ti-doped NaAlH_4 . Similar structures were also found in Ti-doped $\text{NaAlH}_4(010)$ surface, as shown in figure 2. Our calculations showed that desorption of two bottom hydrogen atoms and four side hydrogen atoms caused hydrogen atoms of the neighboring AlH_4^- units to migrate to the Al atoms of the complex. This process is illustrated in figure 3 in which two side hydrogen atoms (H5 and H6) in figure 1(b)) were removed.⁴ After the relaxation, direct bonding interactions between Al atoms in the complex and the neighboring AlH_4^- units starts to develop. This will enable hydrogen migration across different hydrides units. The migration of hydrogen during relaxation after

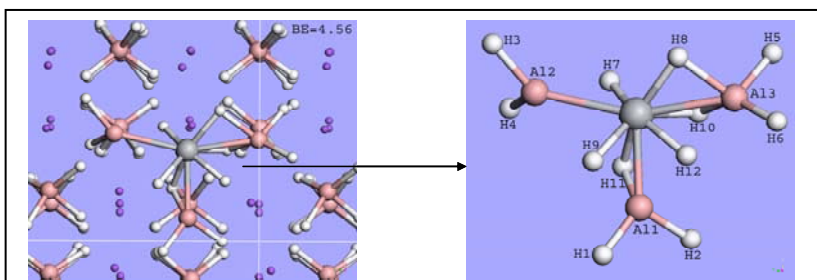


Figure 2. (a) GGA-relaxed structure of Ti-doped $\text{NaAlH}_4(010)$ with Ti in the interstitial space; (b) Detailed local structure of the TiAl_3H_x ($x=12$) complex shown in (a).

desorbing hydrogen indicates that the barrier for hydrogen diffusion across different AlH_4^- units is small. The small diffusion barrier of hydrogen from surrounding AlH_4^- units to the complex structure helps to sustain the hydrogen desorption until the hydrogen in the surrounding region become sufficiently depleted. Complete dehydrogenation will lead to the formation of TiAl_3 dispersed in a predominantly Al phase. Rehydrogenation may start at the dispersed TiAl_3 complex with the formation of TiAl_3H_x complex structure. As the structure became saturated with hydrogen, diffusion of hydrogen from TiAl_3H_x to the neighboring Al site may take place. Alternatively, Ti may migrate to a new Al dominated site and form a new TiAl_3 complex. Hydrogenation will be repeated at the new complex structure. All these arguments support that the TiAl_3H_x complex structure is active in dehydrogenation/hydrogenation processes. Furthermore, this complex does not exclude the presence of Ti hydrides during hydrogenation and reformation of NaAlH_4 . The high desorption energy of two bridging hydrogen atoms bound

to Ti and two side Al atoms may provide explanation of the Ti-hydrides observed experimentally. We are currently working on mapping out the reaction pathways for hydrogen desorption through this complex and determining the transition states and reaction barriers for hydrogen migration and desorption. The understanding from these studies will not only help us to establish the mechanism for this particular system but also to understand the mechanism of similar heterogeneous reactions.

Future Plans

Based on the results obtained in the initial stage of the research, we plan to further explore the role of Ti in hydrogen desorption and adsorption of Ti-NaAlH₄. Our preliminary *ab initio* molecular dynamics (MD) study shows some promising results in this direction. For example, octahedral coordinated Al moieties that may lead to AlH₆⁻ formation were identified during the molecular dynamics runs. More extensive *ab initio* MD calculations would allow us to develop a more complete picture of the potential energy surface. Therefore, we will

- Perform more electronic structural calculations for Ti-doped NaAlH₄ to establish the mechanism of hydrogen desorption.
- Carry out more extensive *ab initio* MD calculations for Ti-doped NaAlH₄ to understand the dynamic nature of the heterogeneous process and to establish a working model for hydrogen desorption/adsorption in complex metal hydrides.
- Extend the research to LiAlH₄ and LiBH₄ and to examine the effect of dopants such as Ti on those complex metal hydrides.
- Examine particle size effect by calculating hydrogen interactions in the clusters of Ti-doped NaAlH₄ with vary sizes.
- Attempt large scale tight-binding MD simulation and/or dynamic Monte Carlo simulation based on the understanding developed at molecular scale.

We hope the understanding achieved through these research activities will help to develop advanced materials with greatly enhanced performance for efficient hydrogen storage.

Publications

- Ge, Q. A first principles analysis of hydrogen desorption from surfaces of LiAlH₄, NaAlH₄, and KAlH₄. Surface Science, submitted.
- Ge, Q. Structure and energetics of LiBH₄ and its surfaces: A first-principles study. Journal of Physical Chemistry A 108, 8682-8690 (2004).
- Liu, J. and Ge, Q. A precursor state for formation of TiAl₃ complex in reversible hydrogen desorption/adsorption from Ti-doped NaAlH₄, Chemical Communication, 2006, DOI: [10.1039/b600679e](https://doi.org/10.1039/b600679e).
- Liu, J. and Ge Q. A first principles study of Ti-catalyzed NaAlH₄: possible active species and its role in hydrogen desorption. to be submitted.

