Role of charge in destabilizing AlH₄ and BH₄ complex anions for hydrogen storage applications: *Ab initio* density functional calculations

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NaAlH₄ and LiBH₄ are potential candidate materials for mobile hydrogen storage applications, yet they have the drawback of being highly stable and desorbing hydrogen only at elevated temperatures. In this letter, *ab initio* density functional theory calculations reveal how the stabilities of the AlH₄ and BH₄ complexes will be affected by reducing net anionic charge. Tetrahedral AlH₄ and BH₄ complexes are found to be distorted with the decrease of negative charge. One H-H distance becomes smaller and the charge density will overlap between them at a small anion charge. The activation energies to release of H₂ from AlH₄ and BH₄ complexes are thus greatly decreased. We demonstrate that point defects such as neutral Na vacancies or substitution of a Na atom with Ti on the NaAlH₄(001) surface can potentially cause strong distortion of neighboring AlH₄ complexes and even induce spontaneous dehydrogenation. Our results help to rationalize the conjecture that the suppression of charge transfer to AlH₄ and BH₄ anion as a consequence of surface defects should be very effective for improving the recycling performance of H₂ in NaAlH₄ and LiBH₄. The understanding gained here will aid in the rational design and development of hydrogen storage materials based on these two systems.

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Of the known systems for hydrogen storage, complex metal hydrides such as NaAlH₄ and LiBH₄ represent very promising candidates. 1–3 AlH₄⁻¹ and BH₄⁻¹ are, however, highly stable thus necessitating high decomposition temperatures. 4,5 Consequently, there has been considerable interest in finding possible destabilization strategies that would facilitate release of molecular hydrogen at lower temperatures. It has been established that a small amount of Ti dopant into NaAlH₄ facilitates accelerated and reversible hydrogen release under moderate conditions. 6–8 A discovery which revitalized the research into complex light-metal hydrides as potential hydrogen storage materials. Theoretically, it has been found that substitution of Na or Al with Ti is energetically feasible and facilitates Al-H bond breaking through the formation of Ti-H bonds. 9,10 However, the Ti-H bond is too strong to break (130 KJ/mol), 11 raising further questions about the catalytic mechanism. Despite many experimental and theoretical studies, the mechanism underlying the enhanced kinetics in Ti-doped NaAlH₄ is not yet fully understood. This remains a key obstacle to developing new materials with improved desorption kinetics and hydrogen storage capacity. 12

More recently, experimental efforts have been directed towards LiBH₄, 13 which has a higher volumetric hydrogen density (18.5 wt %). 14–16 The B-H bond lengths in BH₄⁻¹ are shown to be equivalent by *ab initio* density functional theory (DFT) calculations, in contrast with the experimentally observed geometry, which is strongly distorted. 5 Miwa et al. 5 have proposed that partial substitution of Li⁺ cations with more electro-negative elements, analogous to Ti substitution within NaAlH₄, could be an effective way of lowering the dehydriding temperature of LiBH₄.

A very important objective is to understand the intrinsic role of negative charge in the stabilities of the hydrogen carrying AlH₄ or BH₄ complex anions, since tuning this via various substitution strategies is one of the major current approaches for destabilization. In this study we have utilized state-of-the-art *ab initio* DFT calculations to explore a minimal quantum chemical model that provides new insights into this question and carried out surface calculations in the presence of point defects in order to explore the ramifications of what is learned from the minimal model. In our calculations, we used norm-conserving Troullier Martins pseudo-potentials with BLYP exchange correlation functional 17,18 to describe the ion-electron interaction. Single AlH₄ and BH₄ anions are placed in a cubic cell of 20 × 20 × 20 Å³, and their electronic structures computed as a function of fractional negative charge ranging from −1 to 0. 19 The Kohn–Sham electronic orbitals are expanded in a plane-wave basis and set up to a kinetic energy cutoff 90 Ry. The Tuckerman method 20,21 as implemented in CPMD code 21 is used for decoupling the electrostatic image interaction. Both AlH₄⁻¹ and BH₄⁻¹ anions are calculated to be ideal tetrahedral with constant bond length (1.64 and 1.24 Å for Al-H and B-H bond, respectively) and tetrahedral angle (109.5°). The Mayer bond orders of Al-H and B-H bonds are calculated to be 0.771 and 0.958, respectively. Clearly, B-H bond is primarily covalent and Al-H bond has mixing covalent and ionic bond character. These are collectively in good agreement with other theoretical and experimental results. 5,13,15,22,23

Remarkably, this tetrahedral structure becomes distorted when the anionic charge of the AlH₄ and BH₄ complexes is decreased. Figure 1 presents the variation of Al-H and B-H bond lengths as a function of the reduced anionic charges. It can be seen clearly that the lengths of two Al-H (B-H) bonds are increased from 1.64 to 1.82 Å (1.24 to 1.32 Å), while the remaining two are decreased from 1.64 to 1.52 Å (1.24 to 1.16 Å). Generally, longer chemical bonds imply weaker bond strength. Correspondingly, the H-H distance for the elongated pair in both AlH₄ and BH₄ complexes decreased as...
shown in Fig. 2. This can be understood by the fact that H will form covalent interaction with neighboring H to compensate the reduced anion charge. For the AlH₄ complex, a sharp decrease in H-H distance is observed when the anionic charge varies from 0.2 to zero electrons. The shortest H-H distances very close to the bond length of H₂ are found for the complexes with zero anionic charge, which corresponds to an extreme structural scenario where the complex is surrounded by vacancies, such that it gains no negative charge at all. Charge density plots for four different anionic charges are presented in Fig. 3. Strong overlap of charge density between the elongated H pair indicates that for lower negative charges the activation energy for release of H₂ should be quite small and, thus, the dehydriding temperature can be greatly decreased. We note that the electronic structures for the limiting cases in Fig. 3 with charge −1 and 0 have been validated by MP2 calculations with 6-31+g** basis set for the isolated moieties.

Ti has larger Pauling electronegativity (1.54) than Na (0.93). Hence, the anionic charge of AlH₄ complexes adjacent to a Ti dopant will be reduced and their structures may thereby be distorted as implied by our minimal quantum chemical model above, contributing to enhanced kinetics for H₂ desorption. Substitution of Na is not the only way of modifying the charge on neighboring AlH₄ complexes. Creating a neutral Na vacancy has a stronger effect. Hence, our model also has useful implications for destabilization strategies based on the creation of Na vacancies. Interestingly, while the previous study focused on the removal of H atoms, thereby emphasizing the role of stable AlH₃ complexes, our calculations suggest a mechanism for destabilization of molecular H₂ within the materials, which has potentially greater relevance to the crucial issue of finding low energy reaction pathways for desorption.

As a preliminary exploration of the likelihood of the effects implied by the current minimal model carrying through to the bulk systems, we have also carried out structural optimization for a NaAlH₄(001) surface both in the presence of Na vacancies and for substitution of a Na atom with a Ti atom. The NaAlH₄(001) surface was modeled in a (3×3) surface unit cell containing six layers of Al, total 54 NaAlH₄ molecular units (324 atoms). All the atoms in the bottom two layers were fixed at their bulk position and others are allowed to relax. The vacuum space was larger than 16 Å and...
only gamma point calculation is used for surface Brillouin zone sampling due to the large cell (15×15×32 Å³) we used. All the calculations were performed by using VASP code25,26 and implementing PBE exchange correlation functional27 and the projector augmented wave method.28,29 Structural relaxations were considered to be converged for residual force components are smaller than 0.01 eV/Å. We first found that a single Na vacancy or substituting one Na atom with one Ti atom in NaAlH4 bulk had little effect on the neighboring AlH4 complexes—they are surrounded by other Na⁺ ions and hence retain much of their negative charge. This is in accord with the findings of Ref. 22. However, after introducing point defects, such as a Na vacancy or substituting one Na atom with Ti atom on the NaAlH4(001) surface, we found that the AlH4 units around the defect site are significantly distorted. Both in the case of a Na vacancy and a substituted Ti atom, distortions of the Al-H bond length on the order of 2–3% were observed for AlH4 complexes adjacent to the point defect—some Al-H bonds increasing in length while others decreased. This provided the strong evidence for the upshift and downshift of the Al-H asymmetric stretching modes that are observed by the recent IR experiment.30 In order to check whether the distorted structure around Ti or a single Na vacancy is thermodynamically stable, *ab initio* molecular dynamics (AIMD) simulations are then performed at the experimental temperature (~323 K). The time step is chosen to be 0.5 fs and nuclear deuterium is used instead of hydrogen. We did not observe H2 desorption within the time scale of 2 ps. This suggests that there may be an activation barrier for H2 desorption in both cases.

In marked contrast, however, the presence of two Na vacancies on NaAlH4(001) surface is sufficient to cause a neighboring AlH4 complex to be stripped of its H atoms entirely upon structural optimization, yielding one highly labile H₂ molecule which fills the vacancy space.31 Figure 4(a) presents the initial structure of the NaAlH4(001) surface where two surface Na atoms have been removed (the vertical axis is the z coordinate). Upon relaxation, two H atoms within one AlH4 unit recombined into a H2 molecule as shown in Fig. 4(b). The unstable AlH2 complex will drag one H atom from a neighboring AlH4 complex, with subsequent migration of H vacancies leading to a minimum energy structure with two AlH3 units within the supercell. This is in good agreement with recent findings by inelastic neutron scattering (INS) spectroscopy that show molecular aluminum hydride (AlH₃ or its oligomers) is formed during the early stage of H₂ regeneration of Ti-doped NaAlH₄.32 With reference to the minimal model calculations described above, it is significant that the labile H₂ molecule created in the presence of Na vacancies on the surface comes initially from a single AlH4 complex and is subsequently followed by other H migrations to stabilize the structure. Hence, the conclusions of the minimal model herein do have significant bearing with regard to the low-energy pathways leading to liberation of molecular hydrogen from the surface in the presence of such defects. Most interestingly, we have also observed the spontaneous transfer of atomic H between other AlH₄ units and AlH₃ during the process of geometry optimization [as shown

FIG. 4. Prescribed initial, intermediate and relaxed final configurations for NaAlH₄(001) surface in the presence of two Na vacancies. (a) The starting configuration and (b) The intermediate configuration during geometry optimization (c) The final configuration obtained after full relaxation. The big gray, small gray, small white, big white, and dark balls represent Na, Al, H atoms without obvious change, H atoms to be recombined into one H₂ molecule and H atoms involving H transfer from AlH₄.
in Fig. 4(c)]. Clearly, H (H-vacancy) diffusion in this case should have a very low activated barrier, if any at all. Here, we should emphasize that the minimum distance between vacancies is at least 10 Å so the interaction among periodic images of neutral vacancies is assumed to be negligible. Further calculation based on larger (4×4) surface unit cell gave the same results.

The distorted geometry of BH₄⁻ anions observed experimentally, which contrasts with previous calculations, has been associated tentatively with experimental difficulties in identifying hydrogen positions due to their weak x-ray scattering power. Our calculations indicate a possible alternative rationalization for this phenomenon, since the lithium atom in LiBH₄ bulk is shown to be positively charged with 0.68 electrons (i.e., BH₄⁻⁰.⁶⁸) (Ref. 34) and the presence of neutral Li vacancies or other related defects could cause the anionic charge of BH₄⁻ to be even further suppressed, with neutral Li vacancies or other related defects could cause the structure of AlH₄⁻⁻ to be even further distorted. One H-H distance becomes smaller and the charge density between them will overlap at a small anion charge.

In summary, highly stable AlH₄⁻⁻ and BH₄⁻⁻ can be greatly affected by reducing anionic charge. The ideal tetrahedral structure of AlH₄⁻⁻ and BH₄⁻⁻ complexes becomes strongly distorted. One H-H distance becomes smaller and the charge density between them will overlap at a small anion charge. The activation energies to release of H₂ from AlH₄ and BH₄ complexes are, thus, greatly decreased. The effect is found to be weaker in a BH₄⁻⁻ than in AlH₄⁻⁻ anion due to stronger covalent interaction in a B-H bond than that in an Al-H bond. Our results both further support and help to rationalize the conjecture that the substitution of Na or Li with more electronegative elements, or the creation of neutral Na vacancies, should be an effective way for improving the recycling performance of H₂ in NaAlH₄ and LiBH₄. The understanding gained here can assist the rational design and development of hydrogen storage materials based on these two systems, possibly leading to a breakthrough in industrially viable hydrogen storage technology.

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32See EPAPS Document No. E-PRBMDO-74-034643 for a movie showing the geometry relaxation of the NaAlH₄(001) surface with two neutral Na vacancies. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

