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Effects of Mg and Al doping on the electronic structure and dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$

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ABSTRACT

The electronic structures and bonding characters, the occupation energies of dopants, as well as the formation energies of Frenkel defects in pure $\text{LiBH}_4 \cdot \text{NH}_3$ and in Mg- and Al-substituted $\text{LiBH}_4 \cdot \text{NH}_3$ were investigated by using first-principles calculations. The occupation energies show that the substitutions with Mg and Al destabilize $\text{LiBH}_4 \cdot \text{NH}_3$ and that Mg substitution is easier than Al substitution. Substitution with Mg or Al partly reduced interactions between B–H and N–H atoms, thus improving the dehydrogenation property of $\text{LiBH}_4 \cdot \text{NH}_3$. At the same time, substitution with Mg or Al increases the interactions between metal and N atoms, which stabilize the NH_3 group and inhibit the release of NH_3 during dehydrogenation. The formation energy of Frenkel defects indicates that Mg or Al doping facilitates the formation of Frenkel defects. Our theoretical studies show that Mg and Al are good candidates but Al is better than Mg for improving the dehydrogenation property of $\text{LiBH}_4 \cdot \text{NH}_3$.

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Introduction

Hydrogen, the simplest and most abundant element in the universe, is one of the ideal resources for clean energy. It has become an important subject of research around the world. With the increasing scarcity of oil resources and the continuous deterioration of the environment, hydrogen is recognized as an ideal energy carrier and as a resource with the greatest potential utilization for development [1–4]. It is known as a green energy carrier of the 21st century because of its abundant reserves, high combustion efficiency, and non-pollution. However, its storage is a main impediment to its application.

Development of hydrogen storage materials is the key to solving problems with hydrogen storage technology for hydrogen application. Recent studies have mainly focused on innovation and development of hydrogen storage materials such as metal complex hydrides (AMH_4 , A = Li, Na, K; M = B, Al, Ga). LiBH_4 has the highest hydrogen capacity (18.5 wt%) among these hydrides, but it has high temperature of dehydrogenation and poor reaction kinetics, which hinder the release of hydrogen. To improve the dehydrogenation performance of LiBH_4 , Yu et al. [5] studied the effect of adding various oxides (e.g.: Fe_2O_3). Their results show that LiBH_4 could release large amounts of hydrogen when it is in combination with Fe_2O_3 at 1:2 ratio (quality ratio). There are many experimental studies on the mechanism of hydrogen release

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of $\text{LiBH}_4\text{--MgH}_2$ composites [6–8]. Au et al. [9] revealed that the dopants Mg, MgH_2 , and MgCl_2 dopants could effectively reduce the temperature of dehydrogenation. Orimo et al. [10] performed substitution of Li atoms in LiBH_4 with Mg atoms and found that Mg could reduce the temperature of dehydrogenation. By first-principles calculations, Meng et al. [11] confirmed that H atoms more easily diffuse on the Mg-doped LiBH_4 (010) surface.

Recently, many efforts have been made to study ammonia complexes of metal borohydrides because of their high gravimetric energy density and reasonable dehydrogenation properties. Ammonia complexes of metal borohydrides, $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$ (M = metal), which combine the properties of metal hydrides and ammonia borane, are promising materials for hydrogen storage [12–20]. Among these ammonia complexes, amminelithium borohydride ($\text{LiBH}_4 \cdot \text{NH}_3$) holds the highest hydrogen capacity (18.0 wt%) and is one of the most hydrogen-rich inorganic materials. Since it was first reported 50 years ago [21], the crystal structure and thermal decomposition of $\text{LiBH}_4 \cdot \text{NH}_3$ have been studied in detail. Guo et al. [13] found that $\text{LiBH}_4 \cdot \text{NH}_3$ tended to release hydrogen at high temperature and that the stability of ammonia was the key factor influencing hydrogen release. Therefore, they added MgCl_2 , ZnCl_2 , and AlCl_3 to improve the performance of $\text{LiBH}_4 \cdot \text{NH}_3$. Furthermore, they found that hydrogen release by $\text{LiBH}_4 \cdot \text{NH}_3$ was enhanced in a stable ammonia atmosphere at low temperature, indicating that coordination between NH_3 and LiBH_4 was a key factor influencing dehydrogenation. Meanwhile, several metal hydrides such as LiH, NaH, and CaH_2 were found to be effective in promoting the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ [22]. Wang et al. [23] discussed the structure and decomposition of bimetallic ammine borohydrides $\text{M--Li}(\text{BH}_4)_x(\text{NH}_3)_y$ (M = Li, Mg, Al, and Ca). They found that the $[\text{LiBH}_4]$ group can polarize the molecule and improve the efficiency of dehydrogenation process and purity of released hydrogen from bimetallic ammine borohydrides. Although there are many works focus on the effect of the metal substitution on the dehydrogenation of $\text{LiBH}_4 \cdot \text{NH}_3$ from the experimental point of view, and it has been proven that

defects and impurities play important roles in hydrogen removal and mass transport [24–28], the electronic structure and the bonding nature of atoms in the crystal bulk are still unclear. Therefore, theoretical research on the defect properties of $\text{LiBH}_4 \cdot \text{NH}_3$ is desirable.

In this work, we performed first-principles calculations on $\text{LiBH}_4 \cdot \text{NH}_3$ to predict its fundamental properties, namely, electronic structure, bonding character, occupation energy of dopant, and formation energy of Frenkel defects ($\Delta E_{(\text{Hv}+\text{Hi})}$). Pure $\text{LiBH}_4 \cdot \text{NH}_3$ and Mg- and Al-doped $\text{LiBH}_4 \cdot \text{NH}_3$ were investigated in this study.

Computational methods

Our calculations were performed by using VASP [29] software package, which is based on the generalized gradient approximation (GGA) of the density functional theory, using the projector augmented wave (PAW) to treat the core-valence interaction. The electron exchange correlation energy was described by Perdew–Wang 1991 (PW91) functional [30,31]. The plane-wave cutoff energy of 630 eV was found to be sufficient for pure $\text{LiBH}_4 \cdot \text{NH}_3$ and for Mg- or Al-substituted $\text{LiBH}_4 \cdot \text{NH}_3$. The k points of $9 \times 9 \times 9$ grids were selected through the Monkhorst–Pack method [32]. The convergence criterion for electronic self-consistent iteration was 1×10^{-5} eV. In all structural minimization, ionic positions were allowed to relax with the conjugate-gradient algorithm and a 0.05 eV Gaussian smearing until the residual forces on each atom converge to be below 0.01 eV \AA^{-1} , while the lattice volume and shape were also allowed to change. For the calculation of total energy the tetrahedron method with Blöchl corrections was employed. The total energies of pure metal were obtained by full-relaxing their experimental unit cell. For an isolated hydrogen molecule, its total energy was calculated in a periodic cubic cell of side length of 10 Å with a $3 \times 3 \times 3$ k-point mesh. We did not consider the charge of atoms in the entire framework, that is, atoms were electrically neutral and no background charge was required. For the Mg-

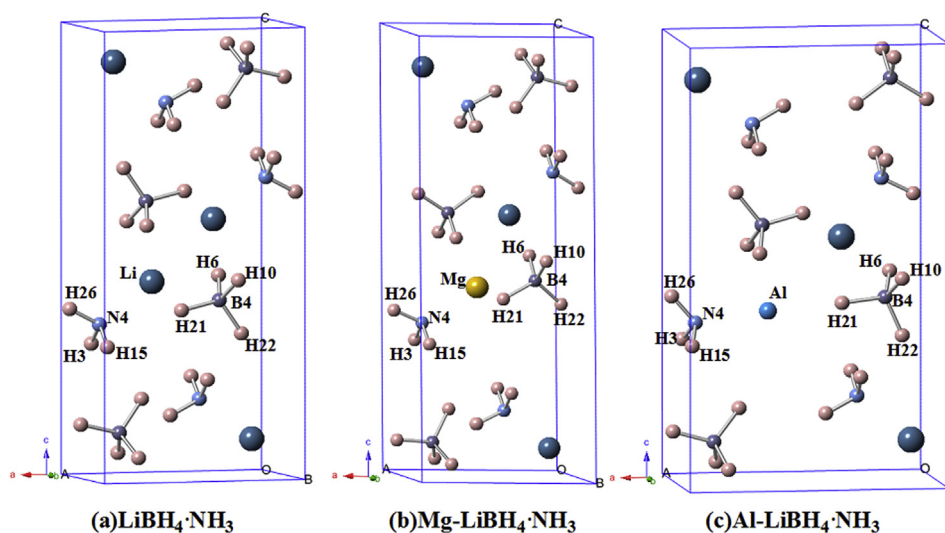


Fig. 1 – Optimized unit cell of pure and Mg-/Al-substituted $\text{LiBH}_4 \cdot \text{NH}_3$. (a) $\text{LiBH}_4 \cdot \text{NH}_3$, (b) $\text{Mg--LiBH}_4 \cdot \text{NH}_3$, (c) $\text{Al--LiBH}_4 \cdot \text{NH}_3$.

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