

First-principles study of intrinsic defects, dopants and dopant-defect complexes in LiBH_4

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Abstract: A first-principles study was reported based on density functional theory of hydrogen vacancy, metal dopants, metal dopant–vacancy complex in LiBH_4 , a promising material for hydrogen storage. The formation of H vacancy and metal doping in LiBH_4 is difficult, and their concentrations are low. The presence of one kind of defect is helpful to the formation of other kind of defect. Based on the analysis of electronic structure, the improvement of the dehydrogenating kinetics of LiBH_4 by metal catalysts is due to the weaker bonding of B–H and the new metal-like system, which makes H atom diffuse easily; H vacancy accounts for a trace amount of BH_3 release during the decomposing process of LiBH_4 ; metal dopant weakens the strength of B–H bonds, which reduces the dehydriding temperature of LiBH_4 . The roles of metal and vacancy in the metal dopant–vacancy complex can be added in LiBH_4 system.

Key words: LiBH_4 ; hydrogen storage material; first-principles calculation; defect; H diffusion; dehydrogenating properties

1 Introduction

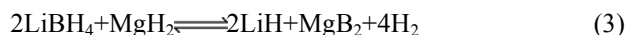
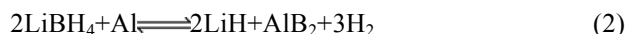
Recently, there has been increased focus on sustainable and renewable energy sources as alternatives to the present use of fossil fuels. Among these energy sources, hydrogen is considered an interesting energy carrier in the future, but the key challenge of safe and efficient on-board hydrogen storage has to be solved before the proposed hydrogen society can become a reality. So for realizing hydrogen energy society, we have to develop high-performance hydrogen storage materials.

A potentially interesting material is the complex metal hydride LiBH_4 , which contains extremely high hydrogen content, 18.4% by mass [1], and partial decomposition of LiBH_4 yields 13.5% (mass fraction) of hydrogen through reaction (1) [2].



However, on-board application of LiBH_4 as a successful solid state reversible hydrogen storage material suffers from problems such as a high operating temperatures (above 370 °C under a hydrogen pressure of 0.1 MPa), slow kinetics and irreversibility after

dehydrogenation due to the chemical inertness of boron [3]. One important approach is to develop a multi component reactive system by incorporating LiBH_4 with elemental metals [4,5] or metal hydrides [5,6]. For example, the onset dehydrogenation temperature for the $2\text{LiBH}_4\text{--Al}$ and $2\text{LiBH}_4\text{--MgH}_2$ systems is reduced to around 593 K [5] because of the change in reaction pathway described by reactions (2) and (3).



The formation of AlB_2 or MgB_2 , instead of pure boron, stabilizes the dehydrogenated state and results in a decrease in ΔH for reaction (2) or (3) relative to reaction (1), and is also beneficial to the regeneration of LiBH_4 . Additionally, a rather high reversible storage capacity is also demonstrated. But the de-/rehydrogenation rates for reactions (2) and (3) are still slow at temperatures below 673 K [5,7]. Another important approach for improving the storage properties of LiBH_4 is to incorporate LiBH_4 with metal halides. AU et al [8] reported that metal halides TiCl_3 , TiF_3 , and ZnF_2 effectively reduced the dehydriding temperature through a cation exchange interaction, and some of the halide doped LiBH_4 is

partially reversible. FANG et al [9] found that TiF_3 exhibits a superior promoting effect of TiCl_3 on the reversible dehydrogenation of LiBH_4 . However, even with the aid of these technologies, the dehydriding/rehydriding properties of LiBH_4 are still far below those required for practical application.

To solve problems mentioned above, it is helpful to understand the mechanisms of the reactions of LiBH_4 with elemental metals, metal hydrides or metal halides. It is well known that chemical reactions must involve mass transport through bulk crystalline materials, so Li, H and B species' diffusion in LiBH_4 is important in hydrogen uptake and release processes. Mass transport can take place only via lattice defects. For example, hydrogen diffusion [10] was found to be vacancy mediated in NaAlH_4 , therefore hydrogen-related defect centers, metal impurity dopants and dopant-defect complexes must play a central role in mass transport processes of LiBH_4 . In the present work, the influence of H vacancy, metal impurity, impurity-vacancy complex on H atoms diffusion and adsorption properties of LiBH_4 systems is studied. Some new results will be beneficial to design the advance Li–B–H based hydrogen storage materials.

2 Computation method and models

LiBH_4 at ambient conditions is an orthorhombic phase with $pnma$ symmetry (24 atoms/unit cell). We first carried out calculations for bulk LiBH_4 to extract basic information about the systems. The calculated lattice parameters are $a=7.2713 \text{ \AA}$, $b=4.4604 \text{ \AA}$, and $c=6.6212 \text{ \AA}$ for orthorhombic LiBH_4 , and the experimental values are $a=7.1786 \text{ \AA}$, $b=4.4369 \text{ \AA}$, and $c=6.8032 \text{ \AA}$ [11]. The calculations of native point defects and metal dopants are performed in a $(1 \times 1 \times 2)$ supercell containing 48 atoms (see Fig. 1). We checked the effect of cell size on the formation of H_v (hydrogen vacancy), M (metal dopant) and $\text{M}+\text{H}_v$ (metal dopant–hydrogen vacancy complex). With a $(1 \times 2 \times 2)$ supercell, we obtained a 0.015, 0.16, 0.067 eV lower formation energy than that with the $(1 \times 1 \times 2)$ supercell (as calculated with Eq. (5) below), which places a tolerable error bar on the formation energies given below.

All the calculations were performed in the framework of density functional theory (DFT) using generalized gradient approximation (GGA) in the version of Perdew–Burke–Ernzerhof [12] and plane–wave pseudopotential method as implemented in the code CASTEP [13]. Ultrasoft pseudopotential represented in the reciprocal space [14] was used for all elements in our models. All the calculations were carried out using a $3 \times 4 \times 2$ Monkhorst-Pack k-point mesh, and the kinetic energy cutoff for the plane wave expansion was set to 270 eV for bulk LiBH_4 , hydrogen-related defects and

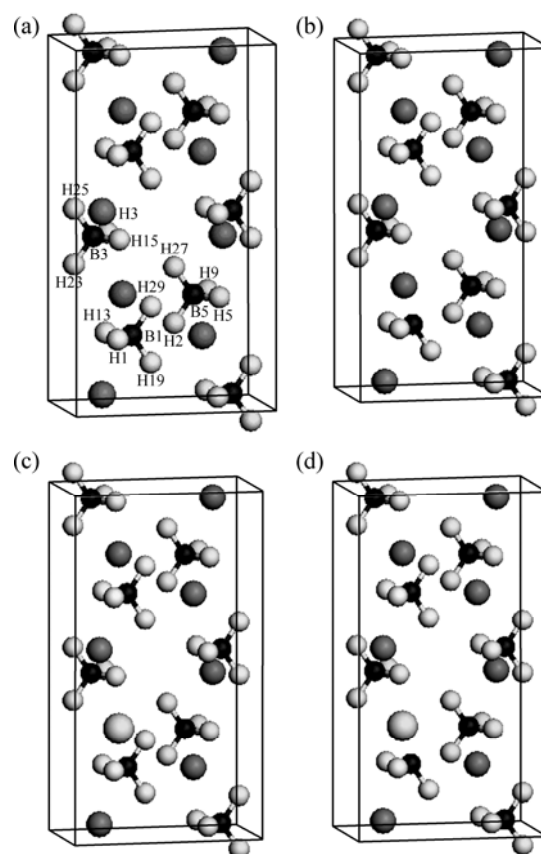


Fig. 1 Models of LiBH_4 (a), LiBH_4+H_v (b), LiBH_4+M (c) and $\text{LiBH}_4+\text{M}+\text{H}_v$ (d) systems (H_v denotes vacancy; M stands for metal dopant Ti, Ni, Zr; large gray spheres are M atoms; large dark gray spheres are Li; small dark spheres are B, and small white spheres are H. Some H and B atoms to be used for discussion are labeled as H1, H3, etc and B1, B3, etc)

dopants, except Ti dopant (set to 280 eV). The convergence with respect to self consistent iterations was assumed when the total energy difference between cycles was less than 1.0×10^{-6} eV. The geometry relaxation tolerance was better than 0.03 eV/ $\text{\AA}$ for force, 0.05 GPa for stress, and $1.0 \times 10^{-3} \text{ \AA}$ for displacement.

One of the most common means of atomic diffusion in crystalline solids is via the vacancy mechanism. Conceptually, it can be broken down into two separate processes: 1) vacancy formation and 2) vacancy–atom exchange.

The formation energy of defect is a crucial factor in determining defect concentration. In thermodynamic equilibrium, the concentration $c(X)$ of a defect X at temperature T is given by [15]:

$$c(X) = N \exp[-E_f(X)/(k_B T)] \quad (4)$$

where N is the number of sites per unit volume at which the defect can be incorporated; $E_f(X)$ is the formation energy of defect X; k_B is Boltzmann constant.

For vacancy diffusion mechanism, vacancy–atom

exchange, atom needs to jump into a vacancy site. So atom must break the bonds and squeeze through its neighbors. So we think that the probability of vacancy–atom exchange depends on the bond strength of atom pair near the vacancy, and the stronger the bond strength is, the larger the probability is.

3 Results and discussion

3.1 Defect formation energy

The formation energy of a defect (H_V , M or $M+H_V$ complex) in $LiBH_4$ is defined as [16]:

$$E_f(X) = E_{tot}(X) - E_{tot}(\text{bulk}) - \sum_i n_i \mu_i \quad (5)$$

where $E_{tot}(X)$ is the total energy of a supercell with a defect; $E_{tot}(\text{bulk})$ is the total energy of the equivalent defect-free supercell; μ_i is the chemical potential of species i (host atoms or impurity atoms); n_i denotes the number of atoms of species i that have been added ($n_i > 0$) or removed ($n_i < 0$). The chemical potential of hydrogen μ_H is fixed at $E_{tot}(H_2)/2$. $E_{tot}(H_2)$ is determined by the optimization of a 1 nm cube with H_2 at eight corners and the bond length of H_2 is estimated as 0.0749 nm. The chemical potential of the dopant is fixed by the energy of the involved elemental solid.

The formation energies of H_V , M and $M+H_V$ complex are listed in Table 1. From Table 1, it can be found that H_V and M all have high formation energies, the formation energy of H_V decreases greatly in the presence of metal dopant, and the formation energy of M also decreases largely in the presence of H_V . The defect formation energy $E_f(X)$ can be used to calculate the defect concentration via reaction (1), so the absolute concentrations of H_V and M are quite low, but once one kind of defect (H_V or M) has been created, the other kind of defect (M or H_V) will be created easily, and therefore the defect concentration in doped or defected $LiBH_4$ will be increased largely. For example, H_V is with lower formation energy in doped $LiBH_4$. Experimentally, additives such as TiO_2 , $TiCl_3$ and ZrO_2 , was found to effectively reduce the dehydrogenation temperature and improve the reversibility of $LiBH_4$. So our calculations are consistent with the experimental observation. Defects

interact with one another and form complexes, such as $M+H_V$ complexes. The complexes also have larger formation energies (see Table 1), thus their concentrations are low.

3.2 Total density of states

The dehydriding/rehydriding processes of $LiBH_4$ involve hydrogen diffusion, and hydrogen diffusion is vacancy mediated. For vacancy diffusion mechanism, to jump into a vacancy site, H atom needs to possess enough energy (thermal energy) to break the B–H bonds, so hydrogen diffusion is closely relative to the bonding behavior of $LiBH_4$. In this section, we analyze the bonding behavior of $LiBH_4$ by the total density of states (TDOS), and in the next section, we will analyze the bonding behavior of $LiBH_4$ numerically by mulliken overlap population.

The calculations for bulk $LiBH_4$ was first carried out to extract basic information about this system. Figure 2 shows the total density of states (TDOS) for $LiBH_4$. The result for the TDOS of bulk $LiBH_4$ is in qualitative agreement with that reported in previous work [16]. The calculated band gap of $LiBH_4$ is 6.7 eV. This value is comparable to that obtained by MIWA et al [17], namely, 6.8 eV. To our knowledge experimental information about the band gap of $LiBH_4$ is not yet available. It is well known that DFT–LDA (local density approximation) or DFT–GGA produces band gaps significantly smaller than the experimental result. So, the experimental value of $LiBH_4$ band gap should be larger than 6.7 eV. The hydrogen diffusion is vacancy mediated, the total density of states for $LiBH_4+H_V$ system $LiBH_4$ with H vacancy was calculated and is shown in Fig. 2 also. It is obvious that there is a defect level created by H_V at just the middle of the gap, and the Fermi level shifts to the middle of the gap. As a result, the behavior of $LiBH_4+H_V$ system likes to be a semiconductor, while the perfect $LiBH_4$ is an insulator. This suggests that H_V like an

Table 1 Formation energies of defects in $LiBH_4$

Complex	$E_f(X)/\text{eV}$						
	H_V	Ti	Ni	Zr	Ti+ H_V	Zr+ H_V	Ni+ H_V
$LiBH_4$	2.4553	3.6414	3.6055	4.1195	3.7929	3.8792	4.7392
$LiBH_4+H_V$		1.3349	2.2812	1.4212			
$LiBH_4+Ti$	0.1515						
$LiBH_4+Zr$	−0.2403						
$LiBH_4+Ni$	1.1337						

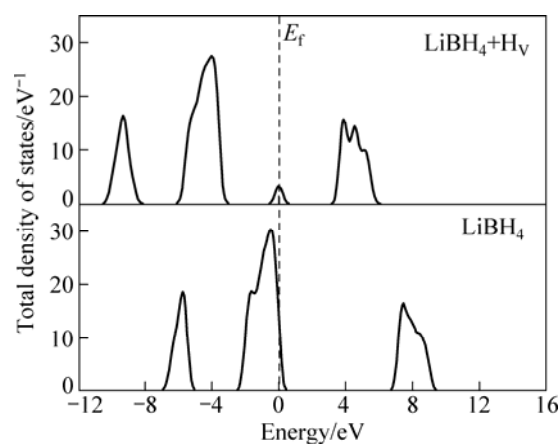


Fig. 2 Total densities of states of $LiBH_4$ and $LiBH_4 + H_V$ systems (H_V denotes vacancy)

electron acceptor pulling electrons from neighbor B—H bond, which leads to changing the distribution of the electrons, and therefore the bond strength of B—H bond near H_V and maybe the diffusion of H atom near H_V .

In $LiBH_4$, metal additives, such as TiO_2 , $TiCl_3$ and ZrO_2 were found to effectively reduce the dehydrogenation temperature of the system [8]. In order to understand the influence of metal additives on the dehydriding/rehydriding processes of $LiBH_4$, the calculations for $LiBH_4+M$ systems ($LiBH_4$ systems with metal dopant) or $LiBH_4+M+H_V$ ($LiBH_4$ systems with metal dopant+H vacancy complex) were carried out. Figure 3 shows the calculated TDOS for $LiBH_4+M$ system ($M=Ti, Zr, Ni$). It can be clearly seen that metal dopants introduce the impurity levels in band gap, the ones induced by Ti and Zr are shallow levels below the bottom of conduction band, while the one induced by Ni is deep level near the middle of the band gap. Ti, Zr and Ni all make the height of binding peak descend (first peak below the Fermi energy), which suggests that the bonding of Li—B or B—H is weakened. The Fermi energy (E_f) level of $LiBH_4+Ti$ (or Zr) system moves into the conduction band, which indicates that the new system of $LiBH_4+Ti$ (or Zr) has the metal-like behavior. The E_f of $LiBH_4+Ni$ system nearly in the middle of the band gap shows that $LiBH_4+Ni$ system has the semiconductor-like behavior. Therefore, from electronic structure point of view, one explanation of the improvement of the dehydrogenating kinetics of $LiBH_4$ by metal catalysts is due to the weaker bonding of B—H in the new system, which makes H atom diffuse easily. We can assume that if any substitution element can reduce the bond strength of B—H and make the system become metal-like, it is most likely a candidate element to improve the dehydrogenating kinetics of $LiBH_4$.

Figure 4 shows the total density of states (TDOS) of $LiBH_4+M+H_V$ ($M=Ti, Zr, Ni$) systems. In order to see

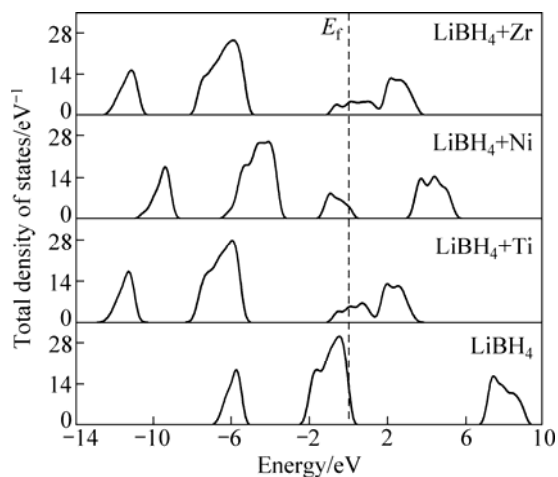


Fig. 3 Total densities of states of $LiBH_4+M$ ($M=Ti, Ni, Zr$) systems

clearly the contribution to defect levels, the local densities of states (LDOS, red lines) of metal atoms are given in Fig. 4. It is clearly seen that there are two kinds of defect levels in the band gap in the presence of dopant-vacancy complex. Compared Fig. 4 with Fig. 3, it can be seen that for $Ti+H_V$ and $Zr+H_V$ complexes, defect levels introduced by Ti and Zr are below the bottom of conduction band and near Fermi level, and H_V introduces the defect levels near the middle of the band gap. For $Ni+H_V$ complex, the level created by Ni is just below the middle of the band gap, while the one created by H_V is just above the middle of the band gap. Fermi levels move into the conduction band for $LiBH_4+Ti+H_V$ and $LiBH_4+Zr+H_V$ systems, but the one of $LiBH_4+Ni+H_V$ system is in the middle of the band gap. In brief, $M+H_V$ complex introduces double defect levels. According to the discussions in the previous section, H_V and M all change the distribution of the electrons, and then change the bond strength of B—H, therefore the presence of $M+H_V$ complex will trigger a significant enhancement in kinetics and hence in dehydrogenation rate of $LiBH_4$ store hydrogen material.

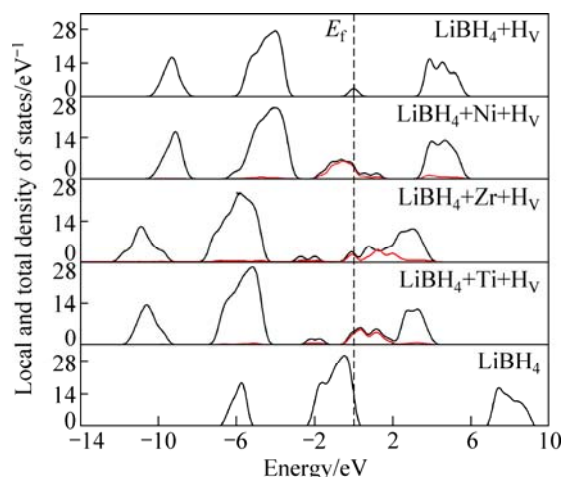


Fig. 4 Local and total densities of states of $LiBH_4+M+H_V$ ($M=Ti, Zr, Ni$) systems

3.3 Mulliken overlap population

To further understand the influence of vacancy, impurity, impurity+ H_V complex on H diffusion, the mulliken overlap population was calculated to analyze the bonding characteristics numerically. Table 2 summarizes the results of the average overlap population. It can be seen that the average population between B—H of perfect $LiBH_4$ is about 0.853 unit bond length (nm^{-1}), indicating the bonding between B—H is strongly covalent.

For $LiBH_4$ with a H29 vacancy, namely $LiBH_4+H_V$ system, the average populations between B1-H1, B1-H13, B1-H19 are 0.890, 0.890, 0.904 respectively, which are larger compared with that of $LiBH_4$. The

Table 2 Mulliken average overlap population analysis for LiBH₄, LiBH₄+M, LiBH₄+H_V and LiBH₄+M+H_V

Bond	Mulliken average overlap population/nm ⁻¹							
	LiBH ₄	LiBH ₄ +Ti	LiBH ₄ +Zr	LiBH ₄ +Ni	LiBH ₄ +H _V	LiBH ₄ +Ti+H _V	LiBH ₄ +Zr+H _V	LiBH ₄ +Ni+H _V
B1-H1	0.853	0.587	0.546	0.699	0.890	0.598	0.491	0.694
B1-H13	0.853	0.587	0.546	0.699	0.890	0.598	0.498	0.694
B1-H19	0.858	0.852	0.845	0.844	0.904	0.813	0.813	0.855
B1-H29	0.869	0.808	0.669	0.813	—	—	—	—
B5-H9	0.853	0.862	0.872	0.854	0.852	0.880	0.881	0.853
B5-H5	0.853	0.862	0.872	0.854	0.852	0.880	0.880	0.853
B5-H21	0.869	0.768	0.803	0.718	0.847	0.768	0.751	0.633
B5-H27	0.858	0.793	0.750	0.842	0.859	0.803	0.795	0.855
B3-H3	0.853	0.845	0.855	0.850	0.852	0.836	0.832	0.860
B3-H15	0.853	0.845	0.855	0.850	0.852	0.836	0.832	0.860
B3-H25	0.869	0.832	0.889	0.816	0.869	0.842	0.880	0.806
B3-H23	0.858	0.777	0.786	0.705	0.850	0.786	0.804	0.698

creation of a neutral hydrogen vacancy by removing one hydrogen atom from a BH₄ unit turns this tetrahedral complex into a trigonal planar BH₃ unit (essentially a BH₃ molecule). AU and JURGENSEN [18] found that a trace amount of BH₃ was released during the decomposing process of LiBH₄. Our calculated mulliken overlap population result shows that B—H bonding in BH₃ unit gets stronger. So it is suggested that BH₃ units in LiBH₄+H_V system could combine and form B₂H₆ molecule which may be emitted during the decomposing process of LiBH₄. From Table 2, it can be seen that the B5-H21 bond of the BH₄ unit at the right side of hydrogen vacancy (BH₃ unit) is weak (the average population is 0.847), so H21 atom can jump to the site of hydrogen vacancy, and therefore H diffusion realizes.

For LiBH₄+M systems (see Fig. 1(c)), the strength of B—H bonds (B1-H13, B1-H29, B1-H13, B3-H23, B5-H27) near M are all weaker than those of the corresponding bonds in LiBH₄, which reduces the dehydrogenating temperature of LiBH₄ with metals or metal halides.

The average populations between B1-H1, B1-H13, B1-H19 of LiBH₄+M+H_V are less than those of LiBH₄ or LiBH₄+H_V, which indicates that B₂H₆ molecule can not form, and B5-H21 bond is also weaker, which is similar to the case in LiBH₄+H_V. So, we can get the conclusion that in the presence of M+H_V complexes, the dehydrogenating temperature of LiBH₄ can be decreased, and the H atom can diffuse easily. From Table 2, we can see that the strength of B—H bonds in LiBH₄+Ni or LiBH₄+Ni+H_V is weaker than that in other metal doped LiBH₄ system. This may explain why some metal additives are more effective than others. By analysis above, we found that the roles of M and H_V in the M+H_V complex can be added in LiBH₄+M+H_V system.

4 Conclusions

The first-principles plane-wave pseudopotential method based on density functional theory was used to study H_V, M, M+H_V complex in LiBH₄. The formation of H_V and M in LiBH₄ is difficult, and their concentrations are low. The presence of one kind of defect is helpful to the formation of other kind of defect. Based on the analysis of electronic structure, the improvement of the dehydrogenating kinetics of LiBH₄ by metal catalysts is due to the weaker bonding of B—H and the new system metal-like, which makes H atom diffuse easily. In addition, based on the mulliken overlap population analysis, it is found that H_V accounts for a trace amount of BH₃ release during the decomposing process of LiBH₄. Metal dopant weakens the strength of B—H bonds, which reduces the dehydrogenating temperature of LiBH₄. The roles of metal and vacancy in the M+H_V complex can be added in LiBH₄+M+H_V system.

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LiBH₄ 中本征缺陷、掺杂剂、掺杂剂–缺陷复合体的第一原理研究

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摘 要: 基于密度泛函理论对储氢材料 $LiBH_4$ 中氢空位、金属掺杂、金属掺杂–空位复合体进行第一原理研究。研究发现氢空位和金属掺杂都不容易实现, 因此它们的浓度都很低。一类缺陷的存在有助于另一类缺陷的形成。基于电子结构的分析, 得出 $LiBH_4$ 中加入金属催化剂导致的释氢动力学性能改善是由于金属催化剂使 B–H 键减弱, 使新体系更具有金属性, 从而使氢扩散更容易; 氢空位是 $LiBH_4$ 分解过程中释放少量 BH_3 的原因; 金属掺杂减弱了 B–H 键, 致使 $LiBH_4$ 的释氢温度降低; 在掺杂–空位复合体中, 金属掺杂剂和空位的作用可以叠加。

关键词: $LiBH_4$; 储氢材料; 第一原理计算; 缺陷; H 扩散; 释氢性质

(Edited by YANG Hua)