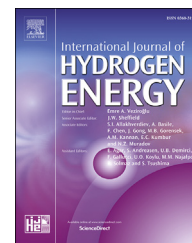




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First principle study of strain effect on structural and dehydrogenation properties of complex hydride LiBH_4

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ABSTRACT

Using the first-principles calculations based on density functional theory (DFT), the structure, stability, thermodynamic and kinetic properties of complex hydride LiBH_4 under different biaxial strains have been investigated. The results show that the free strain LiBH_4 involves a high stability and the biaxial tensile or compressive strain lowers the hydrogen desorption enthalpy of this system. Further, the diffusion activation energy of hydrogen atom in LiBH_4 is also decreased which can accelerate the hydrogenation kinetic of LiBH_4 .

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Introduction

Newly, it has been more focus on sustainable and renewable sources of energy as alternatives to the actual use of fossil fuels [1]. In many ways, hydrogen is the perfect fuel, it is abundant, the most efficient and produces no emissions when used in a fuel cell or combustion engine [2]. However, hydrogen potential has not been realized even partially mainly because up of storage and commercial production difficulties [3–5]. A complex hydride LiBH_4 is a favorable

prospect for solid-state hydrogen storage material capable of releasing the DOE target, because of the attractive volumetric capacity $121 \text{ kg.H}_2/\text{m}^3$, and the highest gravimetric capacity at room temperature exists 18.3 wt% [3,6]. LiBH_4 liberates hydrogen in different reaction step, a partial decomposition of LiBH_4 yields 13.5 wt% [7] of hydrogen through reaction:



The low-temperature desorption for orthorhombic phase liberates only a 0.3 wt% of hydrogen, and LiBH_4 can liberate 13.5 wt% of hydrogen only at high-temperature phase above

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674 K. Further, the rehydrogenation is achieved at 350 bar H₂ and 873 K [8]. High desorption conditions, kinetics, and irreversibility limit his application for hydrogen storage. The formation enthalpy of reaction (equation (1)) is 74 kJ/mol.H₂ and the corresponding entropy of reaction is 115 J/mol.K based on the pressure-concentration temperature (PCT) isotherm measurement [9]. To reduce hydrogen desorption enthalpy several approaches have been performed. The most used approach is the addition of catalysts metal, metal halides [10], oxides [11,12], amides [13] or metal hydride to complex hydride LiBH₄ [14,15]. The addition of oxide SiO₂ to the pure LiBH₄ could reduce hydrogen desorption temperature to 473 K with 10 wt% of hydrogen desorbed [16]. Haizhen Liu et al. [17] assume that hydrogen desorption properties of LiBH₄ can be improved by the addition of Al and AlH₃, and the 2LiBH₄ + AlH₃ composite achieved 11.2 wt% of Hydrogen and the desorption temperature is reduced by more than 303 K. Moreover, mixing the metal hydride MgH₂ with complex hydride LiBH₄ with TiCl₃ catalyst leads to a reversible system which could store 8.1 wt% and reduce relatively hydrogen desorption enthalpy about 25 kJ/mol [18]. The recent approach used is nanoengineering to confine LiBH₄ in Nanoporous [19,20] or mix LiBH₄ with nanotubes [21]. For example, Vajeeston P. et al. [22] reported that is relatively easier to remove hydrogen from the surface of the clusters and nanowhiskers than from bulk crystals and (010) surface is the most stable. Another study of confined LiBH₄ nanoparticles revealed that the reason for the improved (de)hydrogenation effect of nanoconfined LiBH₄ is a chemical interaction between the products and an intermediate compound of LiBH₄ reaction steps [23]. Gross et al. [24] declared that LiBH₄ incorporated within Nanoporous carbon induce to 6.4 wt% of hydrogen desorbed between 573 and 800 K and LiBH₄ rehydrated at 600 K under 100 bar of hydrogen. In order to use Lithium borohydride as an energy carrier in mobile applications, it is necessary to ameliorate the thermodynamics properties of hydrogen storage in LiBH₄ without reducing its high gravimetric capacity (18.3 wt%). In this study, the role of biaxial strain on the particles of LiBH₄ and their effect on the stability, thermodynamic properties, and hydrogenation kinetics was investigated. In section [computational methods](#), the details and methods to perform our calculation are given. Section [Results and discussion](#) is devoted to the presentation, the discussion and the comparison of our numerical results with those obtained experimentally. In the last section, the conclusion is given.

Computational methods

At ambient conditions, LiBH₄ crystallizes in the orthorhombic structure with space group *Pnma* (No. 62) [25], see Fig. 1. The lattice constants are *a* = 7.178 Å, *b* = 4.437 Å, *c* = 6.803 Å. Li, B, H1, H2 and H3 atoms occupy the 4c (0.1568, 0.25, 0.1015), 4c (0.3040, 0.25, 0.4305), 4c (0.900, 0.25, 0.956), 4c (0.404, 0.25, 0.280) and 8d (0.172, 0.054, 0.428) sites respectively [25]. In this structure, each anion [BH₄]⁻ is surrounded by four lithium Li⁺ and each Li⁺ cations surrounded by four anions [BH₄]⁻ in both tetrahedral configurations.

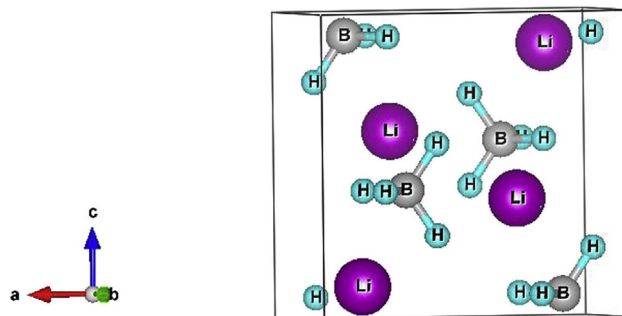


Fig. 1 – Orthorhombic structure (a) and density of state (b) of LiBH₄.

Once the crystalline structure of the unstrained unit cell of LiBH₄ was fully relaxed, the mechanical biaxial strain is imposed on the relaxed LiBH₄ unit cell along x[100] and y[010] directions according to equation (2); [26]:

$$\varepsilon_{xx}(\%) = \varepsilon_{yy}(\%) = \frac{a(b) - a_0(b_0)}{a_0(b_0)} \quad (2)$$

where the lattice constants *a*(*b*) of LiBH₄ unit cell are constrained to several different values, differing from the equilibrium lattice constants *a*₀(*b*₀) by fractions ranging from –6% to 6% by step of 1%. The lattice constant *c* is obtained by allowing all atomic positions to relax to a minimum energy state under each strain. All atomic positions in each strained LiBH₄ unit cell with constrained lattice constants ‘*a*’ and ‘*b*’ were fully optimized to obtain the lattice constant *c* using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [27]. In general, the negative value of $\varepsilon_{xx}(\varepsilon_{yy})$ represents the compression strain state in the *x* and *y*-axes, although the positive value of $\varepsilon_{xx}(\varepsilon_{yy})$ indicates that the model under a tensile strain [28].

All calculations were carried out in the context of density functional theory (DFT). The generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) functional [29] and plane wave pseudopotential method (PWSCF) implemented in the Quantum Espresso code are used to solve the Kohn–Shame equation [30]. Energy cutoff of 50 Ry and *k*-point samplings of 6 × 8 × 6 were used for all the calculations. To ensure a high accuracy in our performed computations, both self-consistent criterions of the energy and the density together with a precision of 10⁻⁸ Ry and 10⁻⁶ Ry respectively were used. Atomic and parameters relaxation was performed with an energy convergence of 10⁻⁷ Ry and a force convergence of 10⁻⁴ Ry per Bohr.

The energies of (un)strained LiBH₄ unit cell are calculated then the desorption enthalpies are deduced from Equation (3):

$$\Delta H_{des} = E_{tot}(B) + E_{tot}(LiH) + \frac{3}{2}E_{tot}(H_2) - E_{tot}(LiBH_4) \quad (3)$$

where $E_{tot}(LiBH_4)$ presents the total energy of strain-free and strained LiBH₄ and $E_{tot}(B)$, $E_{tot}(LiH)$, $E_{tot}(H_2)$ are the total energy of boron, lithium hydride, and hydrogen molecule respectively. The used lattice parameters and the calculated energies are given in Table 1.

The molecule Hydrogen energy $E_{tot}(H_2) = -2.330$ Ry are in good agreement with that obtained by FLOP in Refs. [31,32].

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