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First-principles study of hydrogen vacancies in lithium amide doped with titanium and niobium

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ABSTRACT

The crystal and electronic structures, the formation energy of H vacancies, and the diffusion path of the H atom (i.e., diffusion path of H vacancy) in unsubstituted and substituted LiNH_2 crystal were investigated by periodic first-principles calculations. The bonding characters between atoms were studied by topological analysis of electron density. Our calculations reveal that substitution of the Li atom with Ti or Nb favors the formation of hydrogen vacancies adjacent to substitution, and the existence of an H vacancy and Ti or Nb substitution can cause weakening of nearby N–H bonds, which facilitates N–H bond dissociation. The minimum energy paths of H diffusion show that the substitution can reduce the energy barrier and thus favor H diffusion in the bulk phase of LiNH_2 . Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Energy is the material basis of the survival and development of human society. With the very rapid development of the global economy, the human demand for energy is increasing. However, oil reserves are declining, thus the ongoing search for alternative sources of energy is expected. Hydrogen is an ideal energy carrier because its use does not cause pollution and it has abundant reserves. Hydrogen as a green energy carrier has gained much attention. The wide use of hydrogen for producing clean energy of car fuel in the future has been forecasted [1]. However, the effective use of hydrogen as an energy carrier has been impeded by the difficulty of hydrogen storage.

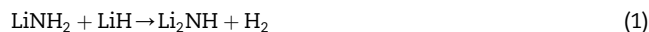
Promising methods for storing hydrogen are pressurization of the gas, its conversion to a cryogenic liquid, adsorption on carbon nanotubes, and conversion to clathrate hydrates and other chemical forms [2–5]. The storage of hydrogen in various materials has been found to be more suitable for fuel applications because of its safety and efficiency and its ease of transport [6,7]. Hydrides of light metals come closest to meeting such practical requirements. Light-metal hydrides, such as $\text{Mg}(\text{NH}_2)_2$ [8], LiNH_2 [9], LiBH_4 [10,11], $\text{Ca}(\text{NH}_2\text{BH}_3)_2$ [12,13], and $\text{Li}_4\text{BN}_3\text{H}_{10}$ [14], which are among the onboard hydrogen storage candidates, have moderate gravimetric and volumetric storage capacity, low cost, and readily available sources. They have the highest potential for use as hydrogen storage materials [15].

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Since the first report by Chen et al. in 2002 [16], the thermodynamics and mechanisms of reversible hydrogen release by metal amides and imides have been extensively studied. In particular, LiNH_2 has attracted considerable attention as a hydrogen storage material [17–19]. This compound releases H_2 according to the following reaction [20]:



The theoretical hydrogen yield of this reaction is 6.5 wt% at typical operating temperatures of 150–350 °C [21]. The reaction enthalpy is 67 kJ/(mol H_2) [22,23], which is close to the theoretical value, 73.6 kJ/(mol H_2) [24]. The reaction in Equation (1) has been shown to proceed in two steps: decomposition of LiNH_2 to release NH_3 and lithium imides, and reaction of NH_3 with LiH to form H_2 [25].



The first step (Equation (2)) has been reported to be the bottleneck of the entire reaction [26]. The conversion process of LiNH_2 to Li_2NH involves Li/H mass transport through bulk crystalline phase. David et al. [27] suggested that the reaction of the intermediates involve substoichiometric phases. Hazrati et al. [28] suggested that the dehydrogenation of lithium amide (LiNH_2) + lithium (LiH) system involves mass transport in the bulk (amide) crystal through lattice defects. Lithium/hydrogen interstitials and vacancies play an important role in mass transport and ionic conduction between LiNH_2 and Li_2NH . Hoang et al. [29] propose that hydrogen interstitials and vacancies are responsible for forming and breaking N–H bonds, which is essential in the Li amide/imide reaction. Miceli et al. [30] noted that the interconversion of LiNH_2 and Li_2NH occurs by diffusion of the charged species H^+ and Li^+ .

Although LiNH_2 has a high hydrogen storage capacity, its use still shows several problems such as high operating temperatures and poor dynamic performance. Much work has been done to render the hydrogenation or dehydrogenation process reversible under practical conditions. Strategies that have been explored include addition of metals, nonmetals, or other substances as catalysts [31–37]. By thermal desorption mass spectroscopy, Ichikawa et al. [32] studied the properties of LiNH_2 with Ni, Fe and Co metals and TiCl_3 dopants. They showed that substitution of Li with highly electronegative elements could reduce the decomposition temperature of LiNH_2 and especially adding TiCl_3 would facilitate the release of hydrogen at lower temperature. Liang et al. [33] used a gas–solid reaction method to synthesize a Li–Mg–N–H complex system. They found that partial substitution of Li by Mg could destabilize LiNH_2 , and the dehydriding temperature decreased with increasing Mg concentration. These observations have been verified by theoretical calculations [34]. A 2:1 mixture of LiNH_2 and CaH_2 under vacuum at 300 °C can be used to prepare a Li–Ca–N–H complex that is able to absorb and desorb hydrogen at lower temperatures [35]. By comparing the formation energies of the dopants on the Li site, Hazrati et al. [28] reported that Mg and Ti can easily be incorporated into LiNH_2 , whereas incorporation of Sc and Ca is thermodynamically unfavorable. Gupta and Gupta [38]

calculated the change of reaction enthalpy with a Cu- or Ni-substituted LiNH_2 , and found that the values of reaction enthalpy decrease, and the influence of Ni is significant. Nakamori and Orimo [39] proposed that alloying elements are useful in changing the structural stability and improving the dehydrogenating properties of the LiNH_2 system.

Based on Hazrati and Ichikawa's results [28,32], Ti has been found that it can easily be incorporated into LiNH_2 , and the addition of TiCl_3 to LiNH_2 – LiH could facilitate the release of hydrogen at lower temperature. NbF_5 and NbCl_5 doping may lower the hydrogen desorption temperature and promote reversible hydrogen storage in $\text{Ca}(\text{BH}_4)_2$ [40]. Therefore, in this work, Ti and Nb were chosen for substitution in LiNH_2 . The effects of H vacancies due to doping of Ti or Nb into the bulk LiNH_2 were also investigated. Here, we focused on clarifying the geometrical and electronic structures and interatomic bonding effect of H vacancies in Ti- or Nb-substituted LiNH_2 . We also explored the hydrogen diffusion process in unsubstituted and Ti- or Nb-substituted LiNH_2 with H vacancies.

2. Computational methods

The first-principles calculations adopted in the present study are based on density functional theory (DFT) [41] using the generalized gradient approximation with the Perdew and Wang (PW91) [42,43] exchange correlation function. We used the projector augmented wave method [44] embodied in the Vienna *ab initio* simulation program (VASP) [45]. The plane wave expansion of the Kohn–Sham orbitals was employed. The cutoff energy was set to 470 eV to attain sufficient accuracy, and the Brillouin zone (BZ) k -point $2 \times 2 \times 2$ grid was applied according to the Monkhorst–Pack scheme [46]. A $2 \times 1 \times 1$ supercell was chosen to model the bulk material. The supercell was optimized in terms of volume and shape, and its internal atomic positions were fully relaxed. During the energy minimizations, the convergence criteria for energy and force were set to 1×10^{-6} eV and 0.05 eV \AA^{-1} , respectively. We did not consider the charge of atoms in the entire framework, that is, atoms were electrically neutral and no background charge was required. The atomic valence electrons considered in the calculations are H $1s^1$, Li $2s^1 2p^0$, N $2s^2 2p^3$, Ti $4s^1 3d^3$, Nb $4p^6 5s^1 4d^4$.

To obtain deeper insight into the bonding nature between atoms in LiNH_2 , we performed a topological analysis of the electron density using a cluster model. The cluster was the $2 \times 1 \times 1$ supercell whose configuration had been optimized by VASP as mentioned above. The cluster was subjected to *ab initio* calculations at the B3LYP/6-31G(*d,p*) level using the Gaussian 03 package [47] to generate the wave functions and density matrix. Afterward, the AIM 2000 program [48] was used to perform the topological analysis of the electron density.

The minimum energy path (MEP) of the hydrogen diffusion process was identified by using the climbing image–nudged elastic band method (CI–NEB) [49,50]. In this method, a chain of images are interpolated between the initial and the final states. By minimizing the energy of this string of images, the MEP is revealed.

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