The role of vacancy, impurity, impurity–vacancy complex in the kinetics of $LiNH_2$ complex hydrides: a first-principles study*

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This paper studies first-principles plane-wave pseudopotential based on density functional theory of hydrogen vacancy, metal impurity, impurity–vacancy complex in $LiNH_2$, a promising material for hydrogen storage. It finds easy formation of H vacancy in the form of impurity–vacancy complex, and the rate-limiting step to the H diffusion. Based on the analysis of the density of states, it finds that the improvement of the dehydrogenating kinetics of $LiNH_2$ by Ti catalysts and Mg substitution is due to the weak bonding of N–H and the new system metal-like, which makes H atom diffuse easily. The mulliken overlap population analysis shows that H vacancy leads to the H local diffusion, whereas impurity–vacancy complexes result from H nonlocal diffusion, which plays a dominant role in the process of dehydrogenation reaction of $LiNH_2$.

Keywords: $LiNH_2$, first-principles calculation, impurity–vacancy complexes, dehydrogenating properties

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1. Introduction

As fossil fuel supplies decrease and world demands for energy increase, one of the biggest challenges that will face humankind in the 21st century is to provide a sustainable supply of energy to the world's population. Hydrogen, which can serve as an energy carrier, is expected to play an increasingly important role in meeting these challenges. For realizing hydrogen energy systems in the near future, we have to establish the energy storage and transportation technologies. One of the key technologies is to develop high-performance hydrogen storage materials.

Since the report of Chen *et al.* in the year 2002,[1] lithium–nitrogen–hydrogen (Li–N–H) compounds have been paid much attention for one of the new hydrogen storage systems. Lithium nitrides can absorb/desorb a large amount of hydrogen in the two consecutive reactions as follows:

$$\begin{aligned} Li_3N + 2H_2 &\leftrightarrow Li_2NH + LiH + H_2 \\ &\leftrightarrow LiNH_2 + 2LiH. \end{aligned} \quad (1)$$

Theoretically, a large amount (10.4 wt.%) of reversible hydrogen is accessible in these two reactions. However, the application of Li_3N as a hydrogen storage medium is greatly hindered by its high operating temperature. The $LiNH_2$ and LiH as starting materials were chosen by Ichikawa *et al.*, and the hydrogenating and dehydrogenating properties of the mixture have been investigated,[2] focusing on the following reaction:

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH. \quad (2)$$

The reason is that reaction (2) can more easily absorb/desorb 6.5% mass of hydrogen due to the smaller enthalpy change (ΔH). But reaction (2) caused by the decomposition of $LiNH_2$ into Li_2NH begins at approximately 423–473 K in vacuum[2] and 550 K in argon,[3] which are still higher than the expected temperature for fuel cell applications. Based on the theoretical and experimental study, it has been found that[4] some elements with larger electronegativity, such as Mg, destabilize $LiNH_2$ by partially substituting Li. Experimen-

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tally, it was also reported that some catalysts, especially titanium compounds such as $TiCl_3$, were effective for improving hydrogen storage kinetics on Li–N–H system. In the year 2005, the catalytic effect of some different type Ti additives on dehydrogenating properties for the Li–N–H system was investigated.[5] The results indicated that the Ti^{nano}, $TiCl_3$ and TiO_2^{nano} doped composites revealed a superior catalytic effect in decreasing the temperature of the hydrogen desorption, no trace of Ti^{nano}, $TiCl_3$ and TiO_2^{nano} in the x-ray diffraction (XRD) profiles was found in these doped composites, which indicates that the uniform distribution of nano particle Ti metal between LiH and $LiNH_2$ plays an important role for catalytic effect. For characterizing titanium based catalysts in the Li–N–H hydrogen storage system, the chemical bonding states of the titanium compounds in the mixture of LiH and $LiNH_2$ were examined by x-ray absorption spectroscopy, the results indicated that the Ti atoms in the titanium compounds had a common electronic (chemical bonding) state.[6]

Although a number of effective metal additives have been identified experimentally, the role played by these additives is not fully understood. It is well known that H diffusion in metal hydrides is important in hydrogen uptake and release processes, and hydrogen-related defect centres must play a ventral role in kinetics for these processes. Hydrogen diffusion[7] was found to be vacancy mediated in $NaAlH_4$. In our group, a first-principles plane-wave pseudopotential method based on the density functional theory (DFT) has been used to investigate the catalytic mechanism of $LiNH_2$ by Ti catalysts.[8] It was found that the stability of the system of $LiNH_2$ is reduced, which originates from the increasing valence electrons at Fermi level (E_f) and decreasing highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap near E_f. The catalytic effect of Ti on the dehydrogenating kinetics of $LiNH_2$ may attribute to the reduction average populations between N–H per unit bond length (nm^{-1}), which leads to the reducing of the chemical bond strength of N–H. In this paper, we shall study the influence of H vacancy, metal impurity, impurity–vacancy complex on H atoms diffusion and adsorption properties of $LiNH_2$ systems. Some new results will be beneficial to design the advance Li–N–H based hydrogen storage materials.

2. The computation method and models

2.1. Method

All the calculations were completed with a first-principles plane-wave psendopotential method (CASTEP software package) based on DFT[9] in which the exchange correlation potential adopts a generalized gradient approximation of Perdew–Burke–Ernzerh form.[10] Ultrasoft pseudopotential represented in the reciprocal space with the Cepeley-Alder exchange–correlation potential[11] was used for all elements in our models. Kinetic energy cut off of 270–310 eV was employed to guarantee a good convergence for total energy and forces acting on the atoms. All the calculations were carried out by using a 4×4×2 Monkhorst–Pack k-point mesh. The convergence with respect to self consistent iterations was assumed when the total energy difference between cycles was less than 2×10^{-6} eV. The geometrical relaxation tolerances were better than 0.05 eV/Å for force, 0.1 GPa for stress, and 2.0×10^{-3} Å (1 Å=0.1 nm) for displacement.

2.2. Crystal structure and models

The crystal structure of $LiNH_2$ is a body-centred tetragonal, structure with space group I-4. The experimental values of lattice constants determined by XRD experiment are $a = b = 0.5031$ nm and $c = 1.0210$ nm, $\alpha = \beta = \gamma = 90°$.[12] We carried out calculations for bulk $LiNH_2$, the calculated lattice parameters are $a = 0.5078$ nm, $c = 1.0281$ nm, which are in good agreement with experimental values. For calculations of metal impurity–vacancy complexes, we used a cell containing 32 atoms by substituting Li with metal M (M=Mg, Ni, Ti) and removing one H atom, the crystal structures of $LiNH_2$, $LiNH_2$ with an H vacancy, Li(M)NH_2, Li(M)NH_2 with an H vacancy are shown in Fig. 1. The valence electron configurations of atoms are Li $1s^22s^1$, Mg$2p^63s^2$, N $2s^22p^3$, H $1s^1$, Ti $3s^2$ $3p^63d^24s^2$, Ni $3d^84s^2$.

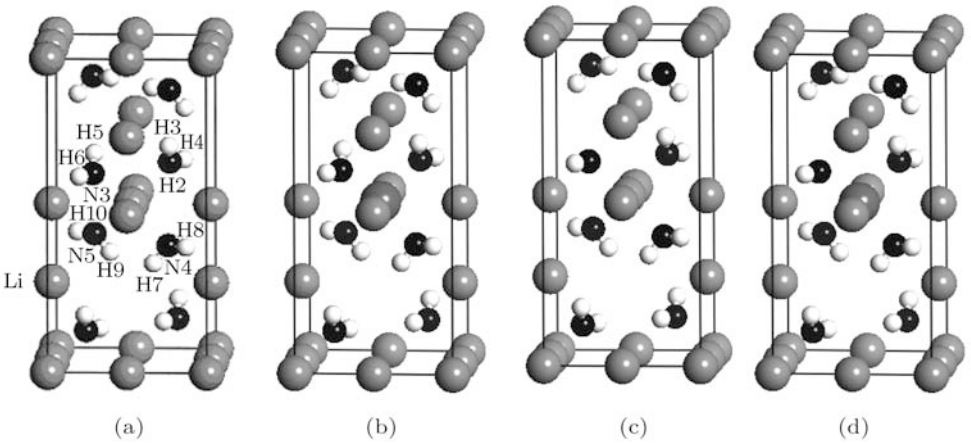


Fig. 1. (a) Models of $LiNH_2$, (b) Li(M)NH_2, (c) $LiNH_2$ with an H vacancy and (d) Li(M)NH_2 with an H vacancy crystal structures. Large dark gray spheres are Ti, Ni, Mg; medium gray spheres Li, small dark spheres N, and smaller white spheres H. Some H and N atoms used for discussion are labeled as H1, H2, H3, H4 and H5, N1, N2, N3 and N4.

3. Results and discussion

3.1. The influence of vacancy, impurity–vacancy complex on H atom diffusion

In thermodynamic equilibrium the concentration $c(X)$ of a defect X at temperature T is given by[13]

$$c(X) = N_{\text{sites}} N_{\text{config}} \exp[-E_{\text{V}}(X)/k_{\text{B}}T], \qquad (3)$$

where $E_{\text{V}}(X)$ is the formation energy of defect X, N_{sites} is the number of lattice sites per unit volume on which the defect can be incorporated, and N_{config} is the number of configurations per site in which the defect can be formed. For vacancy diffusion mechanisms, to jump into a vacancy site, H atom needs to possess enough energy (thermal energy) to break the bonds and squeeze through its neighbours. The energy necessary for motion, E_{m}, is called the activation energy for vacancy motion. The probability of thermal fluctuation needed to overcome the energy barrier (E_{m}) for vacancy motion

$$P = \nu \exp[-E_{\text{m}}/k_{\text{B}}T], \qquad (4)$$

where ν is the characteristic vibration frequency for H migration and E_{m} is the H migration barrier energy. The self-diffusion coefficient of H, therefore, can be estimated to be[14]

$$D = D_0 \exp[-(E_{\text{V}} + E_{\text{m}})/k_{\text{B}}T], \qquad (5)$$

where D_0 is the pre-exponential constant and $E_{\text{V}}+E_{\text{m}}$ is the diffusion activation energy. When the defect formation energies and diffusion activation energies are known, the net diffusion coefficient of H in $LiNH_2$ can be evaluated.

Vacancy formation energies of H atom in $LiNH_2$ and Li$M$$NH_2$ are calculated by[15]

$$E_{\text{V}} = E_{\text{tot}}(\text{LiNH}_2 + \text{V}) - E_{\text{tot}}(\text{LiNH}_2) + E_{\text{tot}}(\text{H}_2)/2, \qquad (6)$$

$$E_{\text{V}}(M) = E_{\text{tot}}(\text{Li}M\text{NH}_2 + \text{V}) - E_{\text{tot}}(\text{Li}M\text{NH}_2) + E_{\text{tot}}(\text{H}_2)/2, \qquad (7)$$

where E_{tot}($LiNH_2$+V) and E_{tot}(Li$M$$NH_2$+V) are the total energy of $LiNH_2$ and Li$M$$NH_2$ supercell model with one H vacancy respectively, V stands for H vacancy. E_{tot}($LiNH_2$) and E_{tot}(Li$M$$NH_2$) are the total energy of $LiNH_2$ and Li$M$$NH_2$ supercell model respectively. The total energy of H_2 molecule $E_{\text{tot}}(H_2)$ is determined by the optimization of a 0.1 nm cube with H_2 at eight corners, and the bond length of H_2 was estimated to be 0.0749 nm. The presence of H vacancy in Li$M$$NH_2$ is equivalent to the presence of impurity–vacancy complex in $LiNH_2$. Vacancy formation energies of $LiNH_2$, $LiMgNH_2$, $LiNiNH_2$, $LiTiNH_2$ are 2.803, –0.895, 0.454, –1.480 eV, respectively. It can be found that H vacancy is formed more easily by the metal (Mg, Ni, Ti) substitution.

For H atom diffusion, we consider the exchange of H10 atom with the adjacent H5 vacancy along the 001 direction. Migration barrier energy for H is calculated by linearly interpolating a set of images between the known initial and final states: for each fixed H atom position, the calculation models are fully relaxed. The values of migration barrier energy (E_{m}) are obtained as the total energy differences between H atoms at

the saddle point and at the initial lattice site.[16] It is calculated by

$$E_{\rm m} = E_{\rm saddle} - E_{\rm lattice}. \quad (8)$$

Migration barrier energy for H vacancy calculated by Eq. (8) is 0.086 eV, which indicates that H vacancy is mobile well below room temperature. This indicates that H vacancy migration is not a bottleneck, but that, the formation of H vacancies is the rate-limiting step.

3.2. Electronic structure

In order to understand the influence of vacancy, impurity and impurity–vacancy complex on H diffusion, we calculated the total density of states (DOS) of $LiNH_2$, $LiNH_2$ with H vacancies, $LiNH_2$with impurity (Mg, Ti, Ni) and $LiNH_2$ with impurity–vacancy complex (Mg–V, Ti–V, Ni–V), the calculated results are shown in Figs. 2, 3 and 4. From Fig. 2, we can see that the total DOS (TDOS) of $LiNH_2$, $LiNH_2$ with H vacancy shows four major peaks in the whole energy range, the existence of H vacancy tends to increase the electron distribution on the top of valence band near Fermi level. This suggests that H vacancy as electron acceptor pulls electrons from neighbouring N–H bond, which leads to the decrease of the bond strength of N–H bond near H vacancy and the increase of the local diffusion of H atom near H vacancy.

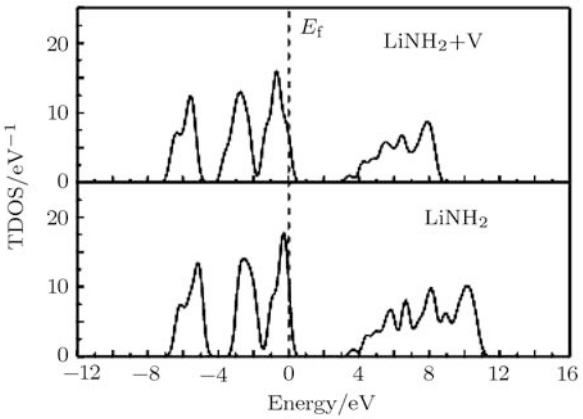


Fig. 2. The TDOS of $LiNH_2$ and $LiNH_2$ with H vacancies (V denotes vacancy).

Figure 3 shows the calculated TDOS for Li$M$$NH_2$ (M=Mg, Ti, Ni), it can be clearly seen that impurities introduce the impurity levels in band gap, the ones induced by Mg, Ti are shallow levels just below the bottom of conduction band. The Fermi energy level $E_{\rm f}$ of $LiNH_2$ doped Mg or Ti moves into the conduction band, which indicated that the new system LiMg(or Ti)NH_2 has the metal-like behaviour. The level induced by Ni is deep level in the centre of the band gap. The $E_{\rm f}$ of $LiNiNH_2$ nearly in the centre of the band gap shows that $LiNiNH_2$ has the simiconductor-like behaviour. The Mg, Ti and Ni all make the height of binding peak descend, which suggests that the bonding between Li–N, and N–H was weakened, but the effect of Ni is not obvious. For vacancy diffusion mechanisms, to jump into a vacancy site, H atom needs to possess enough energy (thermal energy) to break the N–H bonds. Therefore, from electronic structure point of view, one explanation of the improvement of the dehydrogenating kinetics of $LiNH_2$ by Ti catalysts and Mg substitution is due to the weaker bonding of N–H in the new system, which makes H atom diffuse easily. We can assume that any substitution element if it can reduce the bond strength of N–H and make the system become metal-like, it is most likely a candidate element to improve the dehydrogenating kinetics of $LiNH_2$.

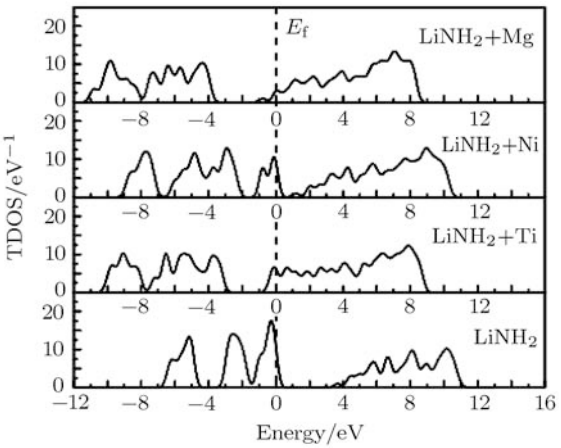


Fig. 3. The TDOS of (LiM)NH_2 (M=Ti, Mg, Ni).

We have also calculated the TDOS of $LiNH_2$ with impurity–vacancy complex, as shown in Fig. 4. It is obvious that an impurity peak appears at Fermi level just below the bottom of conduction band of $LiTiNH_2$+V (V stands for vacancy); the one of $LiMgNH_2$ +V is also near the bottom of conduction band, but its Fermi level moves into the valence band; the impurity peak of $LiNiNH_2$+V is near the centre of the band gap. The H vacancy in the system of $LiNiNH_2$+V, $LiMgNH_2$+V introduces the defect level on the top of the valence band, whereas the one of $LiTiNH_2$+V is not obvious, similar to the vacancy in pure $LiNH_2$. In brief, impurity–vacancy complex introduces double defect levels. According to the discussions in the previous section, H vacancy and metal

impurity all reduce the bond strength of N–H. Therefore, the presence of impurity–vacancy complex will trigger a significant enhancement in kinetics and hence in dehydrogenation rates of $LiNH_2$ store hydrogen material.

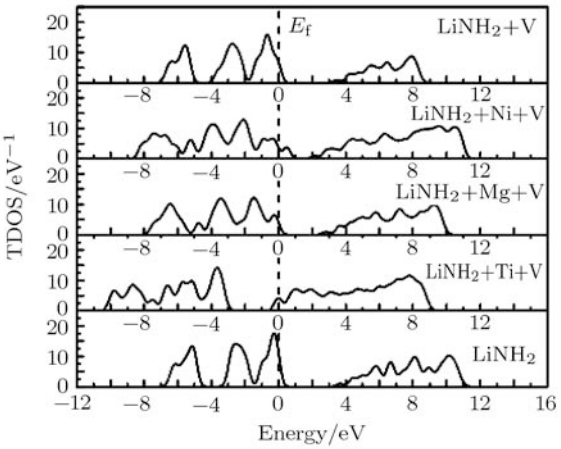


Fig. 4. The TDOS of (LiM)NH_2 (M=Ti, Mg, Ni) with vacancy.

3.3. Mulliken overlap population

To further understand the influence of vacancy, impurity, impurity–vacancy complex on H diffusion, we performed the mulliken overlap population calculation to analyse the bonding characteristics. Table 1 shows the average overlap population for $LiNH_2$, Li(M)NH_2 and their systems with vacancies Li(M)NH_2+V. It can be seen that the average populations between N–H is about 0.807 per unit bond length (nm^{-1}) for $LiNH_2$, indicating the bonding between N–H is strongly covalent. By Mg substitution, the strength of N–H bonds orientating outward in [NH_2] ligands near Mg is weaker than that of the corresponding bonds strength in $LiNH_2$; Ti substitution makes the strength of N–H bonds orientating inward weak; and Ni has little effect. The average population between N3–H6 for $LiNH_2$ with a H5 vacancy is 0.752, which is less than that of in $LiNH_2$. Hence, we can conclude that H vacancy leads to the H local diffusion (within NH_2 ligand). Finally, we turn to the role of impurity–vacancy complexes, from Table 1, it can be seen that not only the strength of N5–H6 bond near H vacancy, but also the strength of N–H bonds (N2–H4 $LiMgNH_2$, N4–H7 and N5–H9 in $LiTiNH_2$) decrease, which results from H nonlocal diffusion between two NH_2 ligands (H diffuses along [010] direction in $LiMgNH_2$, and along [001] direction in $LiTiNH_2$). The formation of Ni–H vacancy complexe has a relatively small impact on H diffusion. It has been found experimentally that Mg destabilizes $LiNH_2$ by partially substituting Li, and nano particle Ti metal has a catalytic role on $LiNH_2$ system, We therefore conclude that H nonlocal diffusion would likely play a dominant role in the process of dehydrogenation reaction of $LiNH_2$.

Table 1. Mulliken average overlap population analysis for $LiNH_2$, Li(M)NH_2, $LiNH_2$ with an H vacancy and Li(M)NH_2 with an H vacancy.

bond	$LiNH_2$	Li(Mg)NH_2	Li(Ni)NH_2	Li(Ti)NH_2	$LiNH_2$+V	Li(Mg)NH_2+V	Li(Ni)NH_2+V	Li(Ti)NH_2+V
N3–H5	0.807	0.795	0.807	0.738	–	–	–	–
N3–H6	0.807	0.686	0.805	0.822	0.752	0.775	0.771	0.796
N2–H3	0.807	0.795	0.811	0.739	0.796	0.826	0.808	0.804
N2–H4	0.807	0.686	0.804	0.791	0.783	0.753	0.814	0.793
N4–H7	0.807	0.795	0.798	0.739	0.796	0.817	0.807	0.727
N4–H8	0.807	0.686	0.783	0.801	0.805	0.798	0.786	0.845
N5–H9	0.807	0.795	0.797	0.738	0.796	0.807	0.805	0.717
N5–H10	0.807	0.686	0.804	0.800	0.806	0.808	0.835	0.843

4. Conclusions

In summary, we have applied first-principles plane-wave pseudopotential method based on DFT to the study of H vacancy, metal impurity, impurity–vacancy complex in $LiNH_2$. Our studies show the easy formation of H vacancy in the form of impurity–vacancy complex, and the rate-limiting step to the H diffusion. Based on our analysis of electronic structure, we have proposed that the possible explanations of the improvement of the dehydrogenating kinetics of $LiNH_2$ by Ti catalysts and Mg substitution is due to the weaker bonding of N–H and the new system being metal-like, which makes H atom diffuse easily. In addition, based on the mulliken overlap population analysis, we found that H vacancy leads to the H local diffusion, whereas impurity–vacancy

complexes results from H nonlocal diffusion, which may play a dominant role in the process of dehydrogenation reaction of $LiNH_2$.

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