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First principles study of the destabilization of Li amide–imide reaction for hydrogen storage

Michèle Gupta[a,*], Raju P. Gupta[b]

[a] *Thermodynamique et Physico-Chimie d'Hydrures et Oxydes, Bât. 415, Université de Paris-Sud, 91405 Orsay, France*
[b] *Service de Recherches de Métallurgie Physique, Centre d'Etudes Nucleaires de Saclay, 91191 Gif sur Yvette Cedex, France*

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Abstract

The chemical compound Li_3N has been proposed as a suitable candidate for the storage of hydrogen since Li is a light element, and thus relatively high weight percent capacities can be achieved. In Li_3N, the hydrogen storage proceeds through the following two-step chemical reaction:

$$Li_3N + H_2 \rightarrow Li_2NH + LiH \quad (1)$$

$$Li_2NH + H_2 \rightarrow LiNH_2 + LiH \quad (2)$$

The theoretical capacity for the combination of both reactions is 10.2 wt.%. The first reaction is, however, highly exothermic with a reaction enthalpy of nearly −145 kJ/mol H_2, and thus requires very high temperatures for hydrogen release. This reaction thus cannot be used for reversible hydrogen storage. With the second reaction alone, the weight percent capacity drops to 6.4 wt.%. This is much lower but still remains acceptable. The reaction enthalpy of reaction (2) has been estimated to be −80 kJ/mol H_2. This is still high and requires relatively high temperatures for hydrogen release. We present in this paper the results of ab initio electronic structure calculations, and show that this reaction enthalpy can be lowered significantly by the substitution of Cu or Ni at the site of Li, the substitution by Ni being more effective.

Keywords: Hydrogen absorbing materials; Electronic band structure; Electronic properties

1. Introduction

For a viable hydrogen fuel in vehicular applications, three main problems need to be tackled; hydrogen storage, hydrogen transport, and finally the hydrogen distribution. The latter two are intimately related to the first. While hydrogen can be stored in its liquid form, the liquefaction process requires considerable amount of energy, and expensive cryogenic tanks operating at very low temperatures are required for hydrogen storage. There is also the problem of leakage of hydrogen from the tanks. Liquid hydrogen is used in space vehicles where such considerations are not important. The storage of hydrogen in its gaseous form poses the problem of well-built cylinders to withstand high pressures with no leakage of hydrogen. Indeed, it is hard to imagine having liquid or gaseous hydrogen in the tanks of cars on the roads where the possibility of hydrogen explosion is the maximum.

The hydrogen storage in the solid form is an alternative which is safe. Considerable amount of work has been done over the last several decades on the intermetallic compounds for hydrogen storage, and $LaNi_5$ has emerged as an intermetallic with optimum properties. It is the intermetallic of choice in portable applications. However, its application in vehicular applications has been hampered by its low weight percent capacity, roughly 1.2%. The hydrogen atoms go into interstitial sites on hydrogenation, and can be easily de-intercalated on de-hydrogenation. Due to the low weight percent hydrogen storage capacity of actual intermetallic compounds, attention has recently been focussed on chemical hydrides of light elements following the work of Bogdanovic et al. [1] on $NaAlH_4$. Recently, Chen et al. [2] proposed that Li_3N can be used for the reversible storage of hydrogen. The hydrogen storage in

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[*] Corresponding author. Tel.: +33 1 69 15 62 28; fax: +33 1 69 15 48 15.
E-mail address: Michele.Gupta@u-psud.fr (M. Gupta).

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this compound occurs through the following two-step chemical reaction:

$$Li_3N + H_2 \rightarrow Li_2NH + LiH$$

$$Li_2NH + H_2 \rightarrow LiNH_2 + LiH$$

Note that in contrast to the case of hydrogen storage in intermetallic compounds where hydrogen interacts with the matrix forming a hydride but keeping the original matrix intact, except for a change in a crystallographic structure in some cases, in the chemical hydrides the hydrogen storage proceeds via a *real* chemical reaction and the formation of a new compound. These chemical hydrides thus present a formidable challenge for reversible hydrogen storage that requires materials with long lifetime and cyclability. In the present case of Li_3N, an interesting theoretical weight percent capacity of 10.2 wt.% can be envisaged if both reactions occurred at reasonably low temperatures. However, the reaction of hydrogen with Li_3N is so strongly exothermic, with a reaction enthalpy of nearly −145 kJ/mol H_2, that extremely high temperatures are needed to get back the hydrogen. The reaction (1) thus cannot be envisaged for hydrogen storage. With reaction (2) alone, the weight percent hydrogen capacity drops to 6.4 wt.%, and the primary reaction for hydrogen storage is not then with Li_3N but with the imide Li_2NH. The reaction of Li_2NH with H_2 is also exothermic with a much lower reaction enthalpy of −80 kJ/mol H_2 compared to reaction (1) but still remains substantial to extract hydrogen at relatively low temperatures. We note here that LiH is a very stable hydride with an enthalpy of formation of −180 kJ/mol H_2, and the decomposition starts at 550 °C. However, combined with $LiNH_2$, the reverse reaction starts at lower temperatures of 300 °C. This still remains a high temperature for purpose of useful applications. Recently, attempts have been made to destabilize the hydrides by mixing with other compounds [3–6]. Some of these reactions are, however, not reversible. We show here that selecting proper substitutions is an alternative route for lowering the reaction enthalpy and that ab initio electronic structure calculations can serve as a guide for this purpose.

2. Methodology

The results presented in this paper were obtained using the Full Potential Linearized Augmented Plane Wave (FPLAPW) method [7] in the Local Density Approximation (LDA) using Hedin–Lundqvist functional [8] for exchange and correlation. Well converged basis sets and a dense grid of k-mesh were employed to obtain total energies converged to better than 0.1 mRy per unit cell. The value of 1.9 Bohr was chosen for the muffin-tin radius at Li and Cu sites, and 0.7 Bohr at the N and H sites. In order to obtain reliable values of reaction enthalpies, both the internal atomic coordinates and the lattice parameters were relaxed. The starting crystal structure lattice parameters and atomic positions were taken from the work of Jacobs and Jura [9] for $LiNH_2$ which is tetragonal, and from Balogh et al. [10], and Herbst and Hector [11] for Li_2NH which was found to be orthorhombic. The relaxed lattice parameters from our calculations turned out to belong to a face-centred-cubic (fcc) lattice with no orthorhombic distortion. However, the use of orthorhombic symmetry does allow the treatment of disordered arrangement of the hydrogen atoms. The calculated lattice parameter and atomic coordinates are in good agreement with previous calculations [11,12].

3. Results

We first discuss the results for the pure imide Li_2NH and the amide $LiNH_2$. The electronic densities of states (DOS) for these two compounds are shown in Figs. 1 and 2 respectively where the partial DOS projected at different atomic sites (PDOS) are also shown. Note that all these densities of states are in units of states per eV per formula unit containing four atoms. These results are quite similar to those obtained in previous calculations [11,12]. For both Li_2NH and $LiNH_2$, we obtain insulating compounds with band gaps of 3 eV. The N s states with small hybridization with H s states, located at energies below −8 eV are not shown. The valence band in both compounds is dominated by the presence of N p-states, strongly hybridized with the H and Li states. In the case of $LiNH_2$, two band gaps can be seen in the valence band. These gaps correspond to the splitting of the p orbitals of N in the amide ion $[NH_2]^-$, and two electrons are accommodated in each splitting. This is not the case with the imide Li_2NH where only one band gap is observed. The first splitting contains two electrons while the upper part holds four electrons. From our total energy calculations, the heat of reaction:

$$\Delta H_R = E(LiNH_2) + E(LiH) - E(Li_2NH) - E(H_2)$$

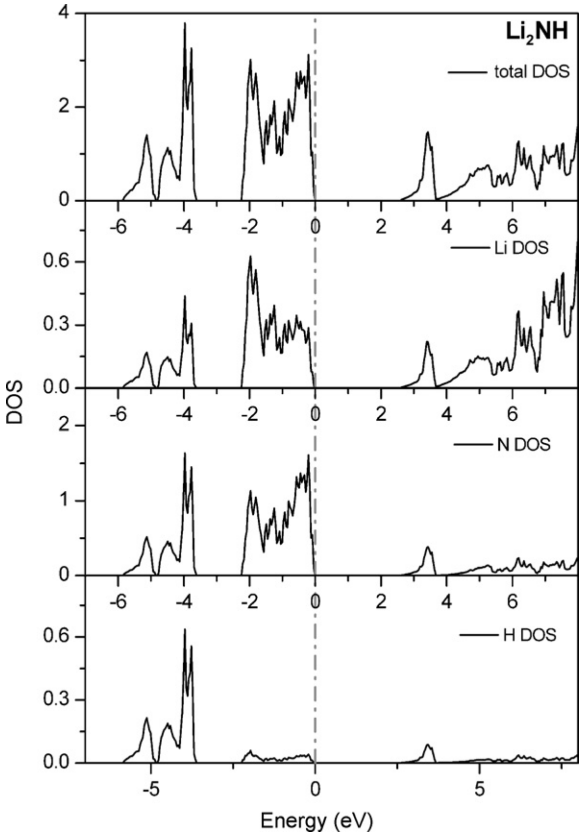

Fig. 1. Total densities of states (DOS) and partial densities of states (PDOS) projected at different atomic sites, all in units of states per eV per formula unit containing four atoms, for the imide Li_2NH. The Fermi level is located at the top of the valence band, and is chosen as the zero of the energy scale.

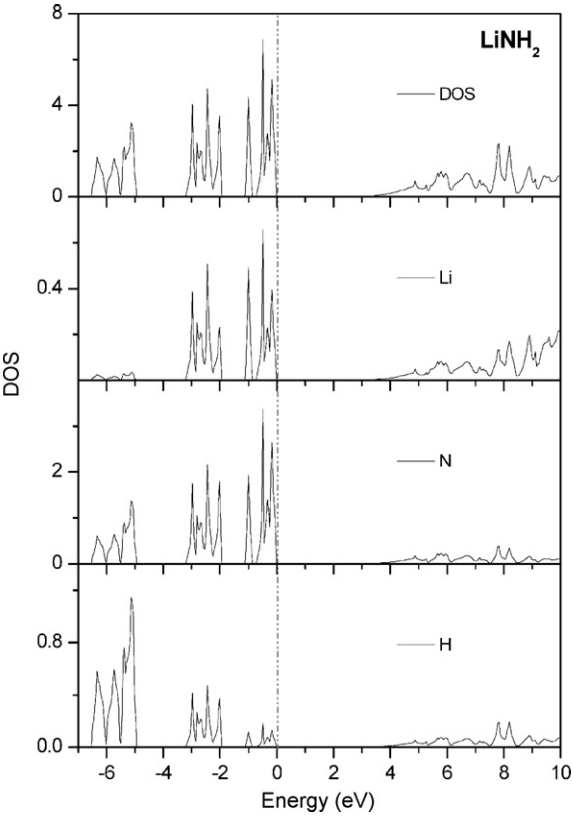

Fig. 2. Total densities of states (DOS) and partial densities of states (PDOS) projected at different atomic sites, all in units of states per eV per formula unit containing four atoms, for the amide $LiNH_2$. The Fermi level is located at the top of the valence band, and is chosen as the zero of the energy scale.

was calculated, and an exothermic value of −0.8953 eV (−84 kJ/mol H_2) was obtained. This is in good agreement with the experimentally estimated value [2] of the heat of reaction. The effect of zero point motion was not included in our calculations since we are primarily interested in the relative shift in the enthalpy of reaction upon substitution at the Li site. In this case, one can safely assume that these corrections are similar since they arise essentially from the motion of the H atoms, and thus cancel out. The calculation of the zero point contribution has been performed in previous work [13].

The DOS and PDOS for the Cu substituted compounds $Li_{1.75}Cu_{0.25}NH$ and $Li_{0.75}Cu_{0.25}NH_2$ are shown in Figs. 3 and 4. We should note here that the changes in the lattice parameters and atomic coordinates are minor due to substitution of Cu at the Li site. This is expected since the ionic radii of Li and Cu are quite comparable. As in Figs. 1 and 2, these DOS and PDOS are in units states per eV per formula unit containing four atoms. In the amide $LiNH_2$, partial replacement of Li by Cu results in the formation of additional states at approximately 2 eV above the valence band maximum. The energy band gap is also reduced to only 1 eV compared to 3 eV in the original material. Although, the majority of the Cu states are located in this new complex, they interact also with N, Li, and H states which are all pushed to higher energies. This upward shift decreases the cohesion in this compound. The interaction of Cu in the imide Li_2NH by the partial replacement of Li by Cu results again in the formation of new states of 2 eV width above the valence band maximum and the reduction of the band gap to 1 eV but the interaction of Cu here is much stronger and the whole valence band is modified. Unlike the case of the amide, it is hard to predict the outcome of such an interaction on the basis of electronic densities of states alone. Our total energy calculations show that the cohesion is lost in this case also but less than in the case of amide. The reaction enthalpy

$$\begin{aligned}\Delta(H_R) &= E(Li_{0.75}Cu_{0.25}NH_2) + E(LiH) \\ &\quad - E(Li_{1.75}Cu_{0.25}NH) - E(H_2)\end{aligned}$$

depends upon the relative decrease of cohesion in the amide with respect to imide. We find that the reaction enthalpy is lowered to −0.76 eV (−71 kJ/mol H_2) due to a greater loss of cohesion in the amide than in the imide. Thus there is a decrease of 13 kJ/mol H_2 in the reaction enthalpy by the substitution of Cu.

Encouraged by these results we have also performed similar calculations for Ni substituting at the Li site. In this case there is a much larger decrease in the reaction enthalpy, which goes down to −0.612 eV (−57 kJ/mol H_2). This value is in the range of practical applications. We note here with the amount of substitutions considered in this work the theoretical weight percent capacity of hydrogen drops from 6.4% to about 5%. The calculations nevertheless show that the substitutions in these

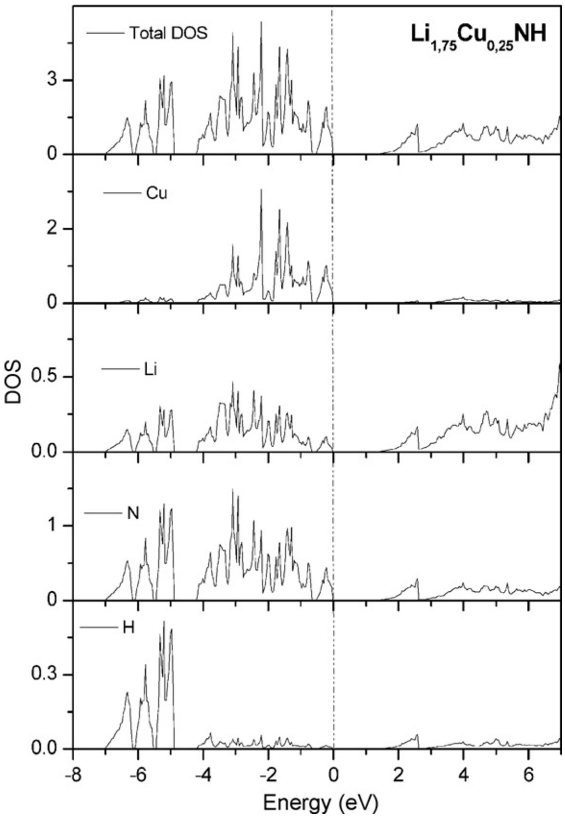

Fig. 3. Total densities of states (DOS) and partial densities of states (PDOS) projected at different atomic sites, all in units of states per eV per formula unit containing four atoms, for the Cu substituted imide $Li_{1.75}Cu_{0.25}NH$. The Fermi level is located at the top of the valence band, and is chosen as the zero of the energy scale.

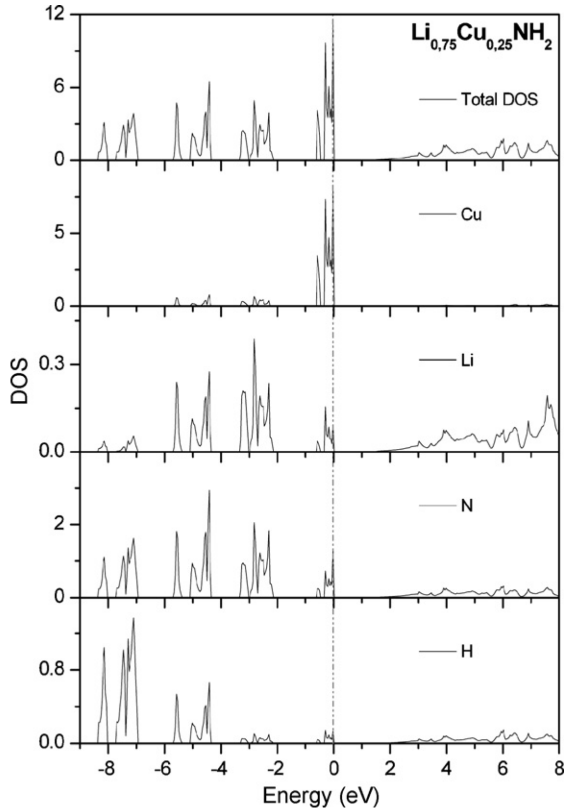

Fig. 4. Total densities of states (DOS) and partial densities of states (PDOS) projected at different atomic sites, all in units of states per eV per formula unit containing four atoms, for the Cu substituted amide $Li_{0.75}Cu_{0.25}NH_2$. The Fermi level is located at the top of the valence band, and is chosen as the zero of the energy scale.

compounds are promising routes to hydride destabilization. We note here that Cu substitution has been attempted theoretically by Miwa et al. [14] in $LiBH_4$ where a similar loss in cohesion was obtained for this compound.

4. Conclusion

Our ab initio electronic structure calculations have shown that a partial substitution by Cu or Ni at the Li the site in the amide or the imide results in the creation of new states above the band gap of these materials. Due to the interaction of Cu or Ni with the other elements in the matrix, some of the states at lower energies in the original compound are brought upward in this new energy window. This results in a loss of cohesion in these compounds. The reaction enthalpy for hydrogenation or de-hydrogenation depends upon the relative loss between amide and imide. In the present case, there is a greater loss in the amide than in the imide. This reduces the reaction enthalpy with both Cu and Ni substitutions. However, Ni seems to be more effective since there is a decrease of nearly 27 kJ/mol H_2 from the original material which brings it near the limit of practical applicability.

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