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Prediction of a new stable compound $\text{Li}_6\text{Mg}(\text{NH})_4$ in the Li-Mg-N-H hydrogen storage system

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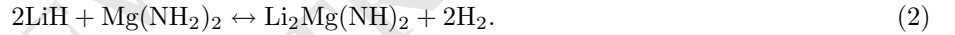
It has been demonstrated that replacing Li_2NH with the mixed-imide $\text{Li}_2\text{Mg}(\text{NH})_2$ improves the reaction conditions for the hydrogen storage system $\text{Li}_2\text{NH} + \text{H}_2 \leftrightarrow \text{LiNH}_2 + \text{LiH}$, at the expense of reducing the gravitational hydrogen capacity from 6.5% to 5.6%. In this article, we report from first-principles calculations a possible new mixed-imide $\text{Li}_6\text{Mg}(\text{NH})_4$ that has less Mg concentration and higher gravimetric capacity for hydrogen storage than $\text{Li}_2\text{Mg}(\text{NH})_2$. We find that $\text{Li}_6\text{Mg}(\text{NH})_4$ is thermodynamically more stable than the phase-separated mixture of $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH over a large temperature range. The reaction $\text{LiH} + 1/4\text{Mg}(\text{NH}_2)_2 + 1/2\text{LiNH}_2 \leftrightarrow 1/4\text{Li}_6\text{Mg}(\text{NH})_4 + \text{H}_2$ can be completed via two steps and releases 6.0 wt% hydrogen in total, at a temperature about 40°C lower than that for the cycling between LiNH_2 and Li_2NH .

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A few years ago, the mixture of LiNH_2 and LiH was introduced as a promising hydrogen storage system¹



This system has attracted considerable attention because, theoretically, the reaction in Eq. (1) releases 6.5 wt% hydrogen at $T < 300^\circ\text{C}$. However, its operational condition was not optimal, with a low decomposition pressure below 1 bar at 285°C . Extensive efforts have been focused on understanding and improving the thermodynamic properties and kinetic barriers associated with the Li-N-H systems.^{2,3} It was realized that replacing lithium amide with magnesium amide could improve the thermodynamics of the hydrogen reaction^{4,5}



The reaction enthalpy in Eq. (2) is 41.6 kJ/mol H_2 ,⁶ significantly lower than that of the reaction in Eq. (1): 66.6 kJ/mol H_2 .⁷ However, the hydrogen capacity of 5.6 wt% is not optimal.

This reduction in the reaction enthalpy is accompanied by simultaneous destabilization of the reactants and stabilization of the products, since $\text{Mg}(\text{NH}_2)_2$ is less stable than LiNH_2 while $\text{Li}_2\text{Mg}(\text{NH})_2$ is more stable than Li_2NH , as can be seen from the calculated formation energies for these compounds.⁸ The stabilization of the products stems from the introduction of vacancies in the mixed-imide $\text{Li}_2\text{Mg}(\text{NH})_2$ by substituting a portion of Li cations with Mg cations in Li_2NH . Similar to Li_2NH , N atoms in $\text{Li}_2\text{Mg}(\text{NH})_2$ form a deformed fcc lattice. But unlike in the conventional anti-fluorite model for Li_2NH where Li atoms fully occupy the tetrahedral sites, Li in $\text{Li}_2\text{Mg}(\text{NH})_2$ occupies one half of the tetrahedral sites of the deformed fcc lattice, Mg occupies another 1/4, and the remaining 1/4 tetrahedral sites are vacant. These vacancies provide natural space to accommodate the N-H bonds. The polar N-H bond prefers to point toward the surrounding vacancies to minimize the electrostatic energy. Indeed, in experimentally and theoretically established models of $\text{Li}_2\text{Mg}(\text{NH})_2$, the tetrahedral vacancies form linear chains and each N-H bond points toward the mid-point of two adjacent vacancies.⁹⁻¹¹

In principle, only 1/8 of the tetrahedral vacancies are needed to accommodate all the N-H bonds since each vacancy can be shared by up to four N-H bonds that are tetrahedrally coordinated around the vacancy. Therefore, the Mg content in the reaction in Eq. (2) could be reduced so that the gravimetric hydrogen capacity will increase while the resulting mixed-imide still experiences a considerable stabilization by the vacancies. Along this line, Michel *et al.* reported a new compound $\text{Li}_4\text{Mg}(\text{NH})_3$, in which 1/6 of the tetrahedral sites are vacant.¹² With the vibrational entropy included, the structure proposed in Ref. 12 is slightly unstable thermodynamically compared with the phase-separated mixture of Li_2NH and $\text{Li}_2\text{Mg}(\text{NH})_2$, although the inclusion of the configurational entropy may make a difference. In this communication, we explore possible new compounds by considering the limiting situation where only 1/8 of the tetrahedral vacancies are created. The proposed structure with a stoichiometry of $\text{Li}_6\text{Mg}(\text{NH})_4$ is energetically preferable with respect to phase separation into Li_2NH and $\text{Li}_2\text{Mg}(\text{NH})_2$. In addition, possible reactions involving this new compound are identified.

An exhaustive search for all possible combinations of lattice vectors and internal coordinates for $\text{Li}_6\text{Mg}(\text{NH})_4$ is computationally challenging even for unit cells containing only one formula unit (15 atoms). In addition, it is highly possible that the primitive cell of the optimal structure contains multiple formula units, which significantly increases the computational cost. A reasonable starting point is the structure of Li_2NH that already contains tetrahedral vacancies.^{13,14} In this model, 1/8 Li atoms are moved from the tetrahedral sites to the octahedral sites, leaving 1/8 of

the tetrahedral sites vacant. The tetrahedral vacancies effectively stabilize the N-H bonds while the Li cations at the octahedral sites increase electrostatic repulsion with neighboring Li cations. Even though other possible arrangements of the interstitial octahedral Li atoms have been proposed by a recent molecular-dynamics simulation,¹⁵ the tetrahedral Li vacancies surrounded by four N-H units is found to be a stable configuration. Based on these structure of Li_2NH with vacant cation sites, the structures for $\text{Li}_6\text{Mg}(\text{NH})_4$ can be formulated by keeping the tetrahedral vacancies and eliminating the energetically unfavorable octahedral Li cations. To balance the charge, we substitute another $1/8$ Li^+ cations with Mg^{2+} cations. The resulting structures after enumerating all inequivalent combinations of Li/Mg on the occupied tetrahedral sites satisfy the stoichiometry $\text{Li}_6\text{Mg}(\text{NH})_4$.

To study the properties of this new compound, we have performed calculations within density functional theory with plane-wave basis as implemented within the VASP package.^{16,17} For the exchange-correlation functional the generalized gradient approximation in the form proposed by Perdew *et al.*¹⁸ is used. The electron-ion interaction is described by Vanderbilt ultrasoft pseudopotentials.¹⁹ A cut-off energy of 600 eV is used for the plane-wave basis. The total-energy converges to 10^{-5} eV in each self-consistent loop, and the structural relaxation terminates when the force on each atom is smaller than 0.01 eV/Å. The free energy at finite temperature is evaluated within the harmonic approximation.

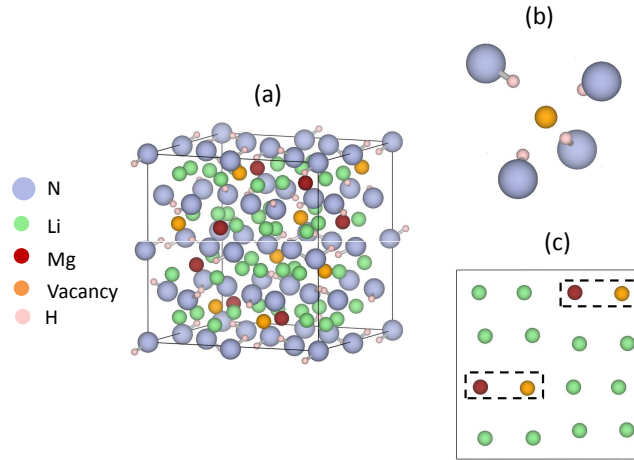


FIG. 1: The lowest-energy structure for $\text{Li}_6\text{Mg}(\text{NH})_4$: (a) the cubic-like supercell, (b) local structure of four N-H bonds tetrahedrally coordinated around a vacancy, and (c) a (100) plane containing the cations and vacancies, with the grouping of Mg and the vacancy indicated.

The formation energy of $\text{Li}_6\text{Mg}(\text{NH})_4$ is defined as its free energy with respect to the phase-separated mixture of $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH :

$$\Delta F = f_{\text{Li}_6\text{Mg}(\text{NH})_4} - f_{\text{Li}_2\text{Mg}(\text{NH})_2} - 2f_{\text{Li}_2\text{NH}}. \quad (3)$$

The free energy of a solid includes the total energy of the electronic system and the vibrational contribution:

$$f = E_{el} + f_{vib}. \quad (4)$$

The vibrational free energy in the harmonic approximation has the form

$$f_{vib} = k_B T \sum_{nk} \ln \left[2 \sinh \frac{\hbar \omega_n(k)}{2k_B T} \right], \quad (5)$$

where n is the mode index for phonons with crystal momentum k . At zero temperature, f_{vib} reduces to the zero-point energy (ZPE) $E_{ZPE} = 1/2 \sum_{nk} \hbar \omega_n(k)$. To obtain the phonon dispersion $\omega_n(k)$, we have calculated the vibrational modes at the Γ point of a 120-atom supercell by diagonalizing the 360×360 force-constant matrix determined by the induced forces due to small displacements of each atom. The Brillouin zone of this large supercell is small enough that Eq. (5) can be evaluated by sampling only the Γ point. Since ΔF defined in Eq. (3) compares the free energy of $\text{Li}_6\text{Mg}(\text{NH})_4$ with the weighted sum of $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH under ambient pressure (the PV term is ignored), the sign of ΔF determines whether $\text{Li}_6\text{Mg}(\text{NH})_4$ is thermodynamically stable with respect to the phase separation. The crystal structures for $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH have yet to be completely determined. Here, we use the lowest-energy structures that have been proposed so far for $\text{Li}_2\text{Mg}(\text{NH})_2$ ¹¹ and Li_2NH ²⁰ to calculate their free energies.

The structure of $\text{Li}_6\text{Mg}(\text{NH})_4$ with the lowest formation energy after enumerating all inequivalent initial configurations is given in Fig. 1 (a) in a cubic-like supercell. The structure has the $Pna2_1$ (No. 33) space group symmetry. The atomic coordinates are given in Table I. As expected, four tetrahedrally coordinated N-H bonds point toward the same vacancy in the relaxed structure as shown in Fig. 1 (b). Figure 1 (c) gives the top view of a (100) plane containing Li, Mg and vacancies, showing that the Mg cation and the vacancy at two nearest-neighbor tetrahedral sites are grouped together because their mutual interaction. Similar local Mg-vacancy pairs also exist in several other structures that have almost identical formation energy as the one shown in Fig. 1. However, the formation energy increases dramatically if the Mg cations and the tetrahedral vacancies are farther apart. This suggests that the local binding between the Mg cation and the vacancy is the dominant factor that determines the formation energy of the structure, while the global arrangement of such Mg-vacancy pairs is not important. Therefore we expect that the local pairing of Mg and vacancies will persist even if one lifts the constraints that we have applied by using a specific structure as the starting point. The formation energy is not expected to change much in a more exhaustive search. The formation energy of the structure in Fig. 1 is -9.1 kJ/mol at 0K with the ZPE included. The formation energy is dominated by the electronic part in Eq. 4, with the vibrational part only contributing a small positive value of 1.0 kJ/mol. This indicates that the vibrational free energy for $\text{Li}_6\text{Mg}(\text{NH})_4$ largely cancels with the vibrational free energy for $\text{Li}_2\text{Mg}(\text{NH})_2 + 2\text{Li}_2\text{NH}$ (see Eq. 3). Figure 2 shows the temperature dependence of the formation energy, which slightly increases to -8.1 kJ/mol at a temperature as high as 600K. These results show that $\text{Li}_6\text{Mg}(\text{NH})_4$ is thermodynamically preferable with respect to the phase separation into $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH .

Structures of $\text{Li}_6\text{Mg}(\text{NH})_4$ with disordered Li, Mg and cation vacancies might be favored by configurational entropy at elevated temperature in a similar way as in the high-temperature disordered phases of $\text{Li}_2\text{Mg}(\text{NH})_2$.^{9,10} The topic of configurational entropy in the general amide/imide system remains an interesting subject for future theoretical studies. For Li_2NH , even the low temperature ground state is not fully resolved. Since we expect that the configurational entropies for the three systems in Eq. 3 will have a cancellation effect similar to that for the vibrational entropy, we do not expect that the configurational free energy contributes to the formation energy much more than the vibrational free energy. Therefore, our current conclusion that $\text{Li}_6\text{Mg}(\text{NH})_4$ is thermodynamically preferable with respect to the phase separation into $\text{Li}_2\text{Mg}(\text{NH})_2$ and Li_2NH is unlikely to change with the inclusion of the configurational entropy.

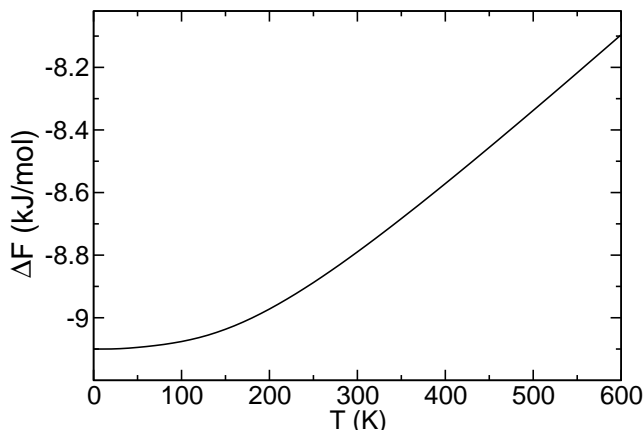


FIG. 2: Formation energy of $\text{Li}_6\text{Mg}(\text{NH})_4$ defined in Eq. (3) as a function of temperature.

The existence of the new stable compound $\text{Li}_6\text{Mg}(\text{NH})_4$ will modify the hydride phase diagram for the Li-Mg-N-H systems discussed previously.^{8,12} Based on the above energetics analysis, $\text{Li}_6\text{Mg}(\text{NH})_4$ will form before the temperature at which the direct reaction between LiH and LiNH_2 in Eq. (1) occurs, if $\text{Li}_2\text{Mg}(\text{NH})_2$ is mixed with LiH and LiNH_2 :



We have also calculated the reaction enthalpy ΔH_0 at 0K and the critical temperature T_c for the reaction in Eq. (6) under ambient pressure. T_c is obtained when $\Delta G = 0$. A semiempirical formula has been used to evaluate the entropy of H_2 in the gas phase following Refs. 8,12. The results are summarized in Table II. When LiH, LiNH_2 , and $\text{Mg}(\text{NH}_2)_2$ are mixed at a molar ratio of 4 : 2 : 1, $\text{Mg}(\text{NH}_2)_2$ will first interact with LiH according to the reaction in Eq. (2) at 118°C; then at a higher temperature of 223°C (still 44°C below the temperature for the direct reaction of LiH and LiNH_2), the product in the reaction in Eq. (2) $\text{Li}_2\text{Mg}(\text{NH})_2$ will react with the remaining LiH

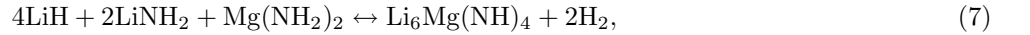
TABLE I: Atomic coordinates of the structure shown in Fig. 1 with the $Pna2_1$ (No. 33) space group symmetry. Lattice parameters are: $a = 7.03$ Å, $b = 10.18$ Å, $c = 7.04$ Å, and $\alpha = \beta = \gamma = 90^\circ$.

Atom	x	y	z
Li	0.995	0.108	0.801
	0.045	0.647	0.760
	0.982	0.878	0.738
	0.252	0.852	0.555
	0.243	0.626	0.500
	0.202	0.097	0.517
Mg	0.250	0.370	0.507
N	0.996	0.755	0.000
	0.000	0.757	0.524
	0.228	0.990	0.766
	0.258	0.502	0.747
H	0.962	0.289	0.626
	0.015	0.297	0.899
	0.359	0.959	0.313
	0.137	0.526	0.240

TABLE II: ΔH_0 (in unit of kJ/mol H_2) and T_c for the reactions studied in this work relevant to the Li-Mg-N-H hydrogen storage system.

Reaction	ΔH_0	ΔH_0 (Ref. 8)	T_c ($^\circ\text{C}$)	T_c ($^\circ\text{C}$, Ref. 8)
(1)	57.2	57.1	267	254
(2)	40.5	35.3	118	96
(6)	52.7		223	

and LiNH_2 according to the reaction in Eq. (6). The net reaction is



which releases 6.0 wt% H_2 . Since further reduction of the Mg content will not provide sufficient vacant cation sites to accommodate all the N-H bonds, $\text{Li}_6\text{Mg}(\text{NH})_4$ also represents the lowest limit of the Mg concentration, and thus the upper limit of the gravimetric hydrogen capacity for the stable hydrogen storage system $\text{Li}_{2(1-x)}\text{Mg}(\text{NH})_x$. It is also noted from Table II that the condition of the original reaction in Eq. (1) is improved more in the reaction in Eq. (2) than in the reaction in Eq. (6). This is because LiNH_2 in the reaction in Eq. (2) is completely replaced by the less stable $\text{Mg}(\text{NH}_2)_2$, while LiNH_2 is still present in the reaction in Eq. (6). Further destabilization of the reactants in the reaction in Eq. (6) is still desirable in the future work.

To summarize, based on first-principles calculations, we predict a new stable mixed-imide $\text{Li}_6\text{Mg}(\text{NH})_4$ that has less Mg content and a better gravimetric hydrogen capacity than $\text{Li}_2\text{Mg}(\text{NH})_2$. The Mg cation and the vacancy tend to group together in the structure of $\text{Li}_6\text{Mg}(\text{NH})_4$ with the lowest energy. $\text{Li}_6\text{Mg}(\text{NH})_4$ is thermodynamically more stable than the phase-separated mixture of Li_2NH and $\text{Li}_2\text{Mg}(\text{NH})_2$ over a large temperature range, and can store 6.0 wt% H_2 , the highest among stable Li/Mg mixed-imides. The conditions for hydrogen release during the reaction involving $\text{Li}_6\text{Mg}(\text{NH})_4$ are also improved compared with the original reaction $\text{LiNH}_2 + \text{LiH} \leftrightarrow \text{Li}_2\text{NH} + \text{H}_2$.

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