# First-principles prediction of high-capacity, thermodynamically reversible hydrogen storage reactions based on $(NH_4)_2B_{12}H_{12}$

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We use a combination of first-principles density functional calculations along with the recently developed grand canonical linear programing method to predict a novel, high-capacity hydrogen storage reaction with thermodynamics suitable for near-ambient reversible storage. Unlike the vast majority of previously proposed complex hydrides, which typically rely on a hydrogen-containing *anionic* unit, our reaction is based on an ammonium-containing hydride, $(NH_4)_2B_{12}H_{12}$, which contains increased storage capacity due to *both anionic and cationic* hydrogen-containing complexes. The predicted decomposition of this hydride is a two-step reaction sequence: $(NH_4)_2B_{12}H_{12} \rightarrow 2BN + \frac{1}{2}B_{20}H_{16} + 6H_2 \rightarrow 2BN + 10B + 10H_2$, which possesses a theoretical gravimetric capacity of 11.3 wt% $H_2$, a single-crystal volumetric density of 52 g $H_2$/L, and $T = 300$ K reaction enthalpies of 17 and 33 kJ/mol $H_2$, respectively, which are well-suited for near-ambient reversible storage. The combination of these three attributes in a single material makes this decomposition reaction sequence highly promising.

The lack of a viable hydrogen storage material serves as a critical bottleneck in the transition to a hydrogen-based economy.[1–4] A practical hydrogen storage material would satisfy several major criteria: (1) a high gravimetric hydrogen storage capacity of at least 6 wt% $H_2$, (2) a high volumetric hydrogen storage capacity of at least 45 g $H_2$/L, and (3) thermodynamics of hydrogen desorption/absorption compatible with near-ambient operating temperatures.[5] There are many examples of materials which possess one or two of these attributes, but it is very rare to find all three in a single material. Hence, there is a significant ongoing world-wide research effort devoted to finding new hydrogen storage materials and reactions.

Complex metal hydrides are a class of solid-state materials actively investigated for hydrogen storage applications. These hydrides are ionic compounds formed between a hydrogen-bearing complex anion—typically $[AlH_4]^-$, $[AlH_6]^{3-}$, $[BH_4]^-$, $[NH_2]^-$, $[NH]^{2-}$, or $[NH_2BH_3]^-$—and a charge-balancing cation, which is usually an alkali metal or alkaline earth metal.[6–12] The selection of anion and cation is the major design variable in any complex hydride. The gravimetric and volumetric capacities of hydrogen are dependent on the weight of the nonhydrogen species in the material versus the amount of hydrogen in the material, which is typically present only in the anionic complex. Although many complex metal hydrides possess high hydrogen capacity, they are often limited by high enthalpies of hydrogen release, which translate into impractically high temperatures for desorption. To date, there are very few materials that have a combination of both high storage capacity (gravimetric and volumetric) and reasonable thermodynamics of $H_2$ release. Therefore, it is of significant interest to identify complex metal hydrides that have all of these characteristics.

In this paper, we use a combination of first-principles density-functional theory (DFT) calculations and the recently developed grand canonical linear programing (GCLP) method[13] to predict a novel, high-capacity hydrogen storage

reaction based on $(NH_4)_2B_{12}H_{12}$ with thermodynamics suitable for near-ambient reversible storage. The $[B_{12}H_{12}]^{2-}$ complex anion has recently garnered attention in the field of complex hydrides as an intermediate decomposition product in several borohydride $X(BH_4)_n$ systems.[3,14–18] The formation of these $X_nB_{12}H_{12}$ *products* in hydrogen release reactions is known to lower the reaction enthalpy, due to the high stability of the $[B_{12}H_{12}]^{2-}$ complex. However, as a *reactant*, the stability of $[B_{12}H_{12}]^{2-}$ units raises the desorption enthalpy, typically making pure phase $X_nB_{12}H_{12}$ compounds unsuitable for hydrogen storage. We can overcome this problem by complexing the $[B_{12}H_{12}]^{2-}$ unit with an ammonium $(NH_4)^+$ cation, with two concomitant benefits: (1) In contrast to most complex hydrides, we propose the use of a hydrogen-bearing cation, which significantly increases the potential hydrogen storage capacity (the ammonium cation is inherently 22.3 wt% hydrogen). (2) The hydrogen decomposition reaction leads to the formation of the low-energy product phase BN, whose stability as a product compensates for the stability of the $B_{12}H_{12}$ reactant. The combination of high capacity and excellent thermodynamics in a single material makes this decomposition sequence highly promising.

We performed first-principles DFT total energy calculations using the Vienna *Ab-Initio* Simulation Package (VASP).[19] The projector augmented wave method was used to obtain all total energies and structural parameters.[20] The electronic exchange and correlation were approximated using the generalized gradient approximation of Perdew and Wang.[21] A plane-wave basis cutoff energy of 875 eV was used in all calculations. For all compounds, Brillouin zones were sampled to convergence on $4 \times 4 \times 4$ Monkhorst-Pack $k$-point meshes or denser. All structural degrees of freedom were relaxed according to the symmetry of the unit cell space group until the forces were less than 0.01 eV/Å and stresses below 0.1 kbar. The energetics of the gas-phase $NH_3$ and $H_2$ molecules were calculated by placing the molecule in a $10 \times 10 \times 10$ Å rectangular box. The phonon frequencies were determined using the frozen

TABLE I. Comparison of calculated and experimental[24] structural parameters of $(NH_4)_2B_{12}H_{12}$, which has space group $Fm\bar{3}$ #202. The lattice constant $a$ is in angstroms, and $(y,z)_i$ are the cell-internal positions for atom $i$.

| Property | Wyckoff | Experiment (XRD) | DFT (VASP) |
|---|---|---|---|
| $(x)_N$ | 8c | 0.250 | 0.250 |
| $(y,z)_B$ | 48h | (0.1329, 0.0819) | (0.1312, 0.0807) |
| $(y,z)_{H1}$ | 48h | (0.2232, 0.1364) | (0.2246, 0.1372) |
| $(x)_{H2}$ | 32f | 0.205 | 0.196 |
| $a$ | | 10.8781 | 10.984 |
| $V$ | | 1287.24 | 1325.128 |

phonon supercell approach where all symmetry-inequivalent rows of the dynamical matrix were calculated by displacing the ions for a total of five 0.03 Å steps around the equilibrium positions and fitting the resulting forces with a third-order Chebyshev polynomial. For all bulk compounds, we used supercells consisting of 54 atoms or more. In previous studies it was found that if there are at least 50 atoms in the supercell, then the vibrational energetics are converged.[22] Vibrational enthalpies and entropies were obtained by summing over the frequencies of the normal modes.[23]

We begin with a comparison of the DFT-relaxed and experimental crystal structures for $(NH_4)_2B_{12}H_{12}$. The crystal structure of $(NH_4)_2B_{12}H_{12}$ was originally determined by Tiritiris and Schleid.[24] It exhibits the antifluorite crystal structure in the $Fm\bar{3}$ space group, with the $[B_{12}H_{12}]^{2-}$ anionic units on a face-centered cubic (FCC) lattice, where the ammonium cation complexes occupy the tetrahedral voids (see Fig. 1). It is pseudomorphic to the prototype $K_2B_{12}H_{12}$ candidate structure, with the potassium cation replaced with the ammonium complex cation. The ammonium cations are fourfold coordinated and oriented such that the hydrogens point toward the center of the neighboring anionic complexes. As a validation of our approach, we find good agreement between the DFT-relaxed structural parameters and experimental data (Table I), giving us confidence that DFT is well poised to study this material.

We next turn to the calculation of reaction thermodynamics. We begin by performing DFT calculations for the energetics, phonon frequencies, and vibrational free energies of all the known stable B-N-H phases in the Inorganic Crystal Structure Database. The list of phases is the following: $(NH_4)_2B_{12}H_{12}$, $H_2$, $N_2$, $NH_3$, B, BN, $BH_3NH_3$, $B_{10}H_8(N_2)_2$, $BH_3N_2H_4$, $B_3N_3H_6$, $(BH_2NH_2)_3$, $(BH_2NH_2)_x$, $(BHNH)_x$, $B_9H_{15}$, $B_8H_{12}$, $B_6H_{10}$, $B_5H_9$, $B_5H_{11}$, $B_4H_{10}$, $B_{20}H_{16}$, $B_{18}H_{22}$, $B_{16}H_{20}$, $B_{13}H_{19}$, $B_{12}H_{16}$, $B_{10}H_{14}$, $(B_5H_8)_2$, and $(B_{10}H_{13})_2$. We also include a hypothetical $(NH_4)_2B_6H_6$ compound, based on the existence of the analogous $K_2B_6H_6$ crystal structure.[25]



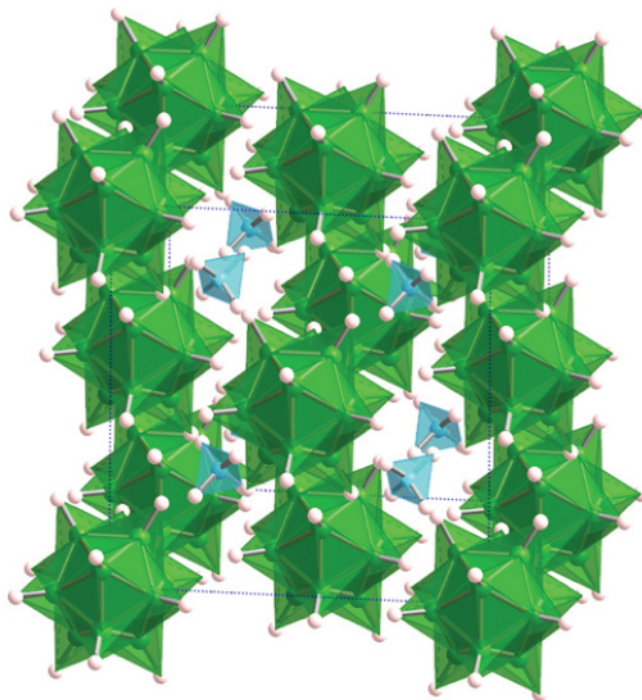FIG. 1. (Color online) Crystal structure of the $(NH_4)_2B_{12}H_{12}$ compound.

Using this database of DFT thermodynamic data, we apply the grand canonical linear programing[8] method to determine the lowest free-energy hydrogen desorption reactions and associated equilibrium thermodynamics. GCLP rigorously identifies the thermodynamically stable phases of a system at a given temperature and pressure by minimizing the grand canonical free energy of a collection of multiphase solids in contact with a hydrogen reservoir. By noting a change of stable phases at different temperatures, GCLP elucidates the thermodynamically preferred reaction pathways of the system, without the need for guesswork or chemical intuition. More details on GCLP can be found in Ref. 8. GCLP has been successfully utilized to determine correct reaction pathways in several multicomponent hydrogen storage systems.[3,8,26–28] By using this combination of DFT energies, vibrational free energies, and GCLP, we find that $(NH_4)_2B_{12}H_{12}$ decomposes in the two-step reaction given in Table II. An intermediate $B_{20}H_{16}$ phase is thermodynamically stable in the decomposition sequence of $(NH_4)_2B_{12}H_{12}$ at a little over 6 wt% of $H_2$ desorption, resulting in a complete decomposition in a two-step reaction with standard state enthalpies of 17 and 33 kJ/mol $H_2$, releasing a total of 11.3 wt% $H_2$.

TABLE II. Thermodynamic data for the decomposition of $(NH4)_2B_{12}H_{12}$. $T_c$ gives the equilibrium temperature at an $H_2$ pressure of 1 bar, and $\Delta S$ is the standard-state reaction entropy.

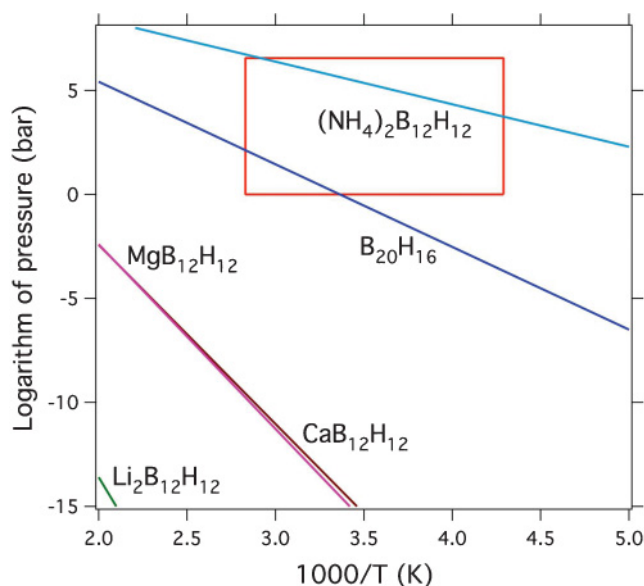| Reaction | wt% $H_2$ | $\Delta H^{static}$ (kJ/mol $H_2$) | $\Delta H^{0K}$ (kJ/mol $H_2$) | $\Delta H^{300K}$ (kJ/mol $H_2$) | $\Delta S^{300K}$ (J/mol K) | $T_c$ (°C) |
|---|---|---|---|---|---|---|
| $(NH_4)_2B_{12}H_{12} \rightarrow 2BN + \frac{1}{2}B_{20}H_{16} + 6H_2$ | 6.76 | 41 | 12 | 17 | 104 | −120 |
| $B_{20}H_{16} \rightarrow 20B + 8H_2$ | 6.90 | 50 | 27 | 33 | 111 | +20 |

FIG. 2. (Color online) Calculated van't Hoff plot for reactions listed in Table II. The region within the rectangular box corresponds to desirable temperatures and pressures for onboard hydrogen storage: pressures from 1 to 700 bar and temperatures from $-40$ to $+80\,°C$. We also show the calculated van't Hoff lines for $X_nB_{12}H_{12}$ compounds with simple metal cations.[3]

One drawback of nitrogen-containing hydride materials is the possibility of $NH_3$ release, which is a well-known poison for proton exchange membrane (PEM) fuel cells.[29] Using the static $T = 0$ K DFT energies, we investigate the relative energetics of reactions involving the release of $H_2$ and those releasing $NH_3$. In order for a reaction to be thermodynamically preferred, the product phases must be lower in energy than a linear combination of the energetics of any two other sets of stable phases. We find that the ammonia gas reactions do not satisfy this criterion and are therefore not thermodynamically stable at low temperature. At higher temperatures, the entropy of the gas-phase species will begin to dominate the thermodynamics. In order to determine the stability at higher temperatures, we may simply compare the number of moles of $H_2$ vs $NH_3$ released in the various reactions. Because there are fewer moles of $NH_3$ than of $H_2$ released, we conclude that even at higher temperatures, the hydrogen release reactions are entropically favored over ammonia release reactions. However, we must acknowledge the possibility of $NH_3$ release being kinetically (as opposed to thermodynamically) favored over $H_2$ release. Future experiments to test the gas-phase release from this material would be of considerable interest.

The thermodynamics of our predicted reaction are quite unexpected for a $B_{12}H_{12}$ containing reactant. It has recently been reported that pure $X_nB_{12}H_{12}$ (for $X =$ Ca, Li, Mg) hydrides are exceptionally stable, decomposing at over 70 kJ/mol $H_2$.[3]

This strong stability manifests itself in a van't Hoff plot (of $\ln P$ vs $1/T$) as a very low pressure and high temperature for $H_2$ release (see Fig. 2). However, these exceptionally stable reactants can effectively be "destabilized" by the formation of a stable low-energy intermediate decomposition phase.[30] For example, $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ form low-energy metal-boride decomposition products, which lower reaction enthalpies compared to $Li_2B_{12}H_{12}$, which forms the higher energy LiH decomposition product. In the $(NH_4)_2B_{12}H_{12}$ reaction, the reactant is destabilized by forming the stable BN phase as a product. The strong stability of BN significantly lowers the reaction energetics, compared to other pure phase $X_nB_{12}H_{12}$ compounds (Fig. 2).

The significant aspect of $(NH_4)_2B_{12}H_{12}$ that leads to its high hydrogen capacity is the inclusion of a hydrogen-containing complex cation. Because complex hydrides typically contain cations merely to balance the charge, they are "dead weight" and contribute nothing to the hydrogen storage capacity of the material. The inclusion of the ammonium cation greatly enhances the capacity, since $NH_4$ is inherently 22.3 wt% $H_2$. We note that our ammonium-based hydrogen storage reactions are based on known, experimentally synthesized materials. Hence, we assert that hydrogen-containing cations should be more generally considered as candidates with complex anions, and that resulting combinations have the potential to uncover promising new hydrogen storage reactions.

In summary, we have used a combination of first-principles DFT calculations with the GCLP method to predict a novel complex hydride reaction based on $(NH_4)_2B_{12}H_{12}$. We find that the thermodynamically preferred reaction is two steps, liberating 11.3 wt% hydrogen with reaction enthalpies of 17 and 33 kJ/mol $H_2$. One must remember however, that while excellent reaction thermodynamics are a necessary condition for hydrogen storage, it is not a sufficient condition. A truly practical hydrogen storage reaction will also have excellent kinetics. For a reaction such as the one proposed here with promising thermodynamics and storage capacity, it is worthwhile to devote considerable effort to optimizing its kinetics and reversibility. Because BN plays a key role in this reaction, kinetics could be improved by catalyzing BN formation, possibly through seeding or alloy catalysts.

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