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Review

# Boron- and nitrogen-based chemical hydrogen storage materials

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ABSTRACT

Boron- and nitrogen-based chemical hydrides are expected to be potential hydrogen carriers for PEM fuel cells because of their high hydrogen contents. Significant efforts have been devoted to decrease their dehydrogenation and hydrogenation temperatures and enhance the reaction kinetics. This article presents an overview of the boron- and nitrogen-based compounds as hydrogen storage materials.

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## 1. Introduction

Hydrogen is a globally accepted clean fuel. The use of hydrogen fuel cells in portable electronic devices or vehicles requires lightweight hydrogen storage or on-board hydrogen generation. For vehicular applications, the U.S. Department of Energy (DOE) has set storage targets; the gravimetric (volumetric) system targets for near-ambient temperature (from −40 to 85 °C) and moderate pressure (less than 100 bar) are 6.0 wt.% (45 g/L) for the year 2010 and 9.0 wt.% (81 g/L) for 2015 [1]. Although there have been a large number of reports on hydrogen storage materials, such as metal hydrides [2] and metal organic frameworks [3], and on on-board reforming of hydrocarbon into hydrogen [4], big challenges still remain. For hydrogen storage materials, the gravimetric and volumetric hydrogen capacities must be improved, whereas for the on-board reforming, the difficulty in operating the system at high temperature poses an obstacle to its practical application. Chemical hydrogen storage materials, due to their high hydrogen contents, are expected as potential hydrogen sources for fuel cells. Among them, boron- and nitrogen-based compounds, such as $LiNH_2$–LiH and $NaBH_4$, have attracted much attention [5–7]. Ammonia borane, $NH_3BH_3$, which has a hydrogen capacity of 19.6 wt.%, exceeding that of gasoline, has made itself an attractive candidate for chemical hydrogen storage applications. Intensive efforts have been made to enhance the kinetics of the hydrogen release from this compound from both solid and solution approaches [8–17]. Hydrazine, $N_2H_4$, with the hydrogen capacity of 12.6 wt.%, is another potential hydrogen carrier. Group VIII metal-based catalysts have been reported to actively enhance the decomposition of this compound to generate hydrogen at room temperature with the by-product of $NH_3$ [18].

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The present review gives a brief survey of the boron- and nitrogen-based chemical hydrogen storage materials.

## 2. Boron-based chemical hydrogen storage materials

Boron-based chemical hydrogen storage materials such as borohydrides (e.g., $LiBH_4$ and $NaBH_4$) and ammonia borane, $NH_3BH_3$, are very promising compounds as hydrogen storage materials because of their high hydrogen capacities. However, practical application of these hydrogen storage materials is now still a big challenge which results from kinetic and/or thermodynamic limitations. Various approaches have been taken to decrease the dehydrogenation and hydrogenation temperatures and to enhance the reaction rate. Some developments are described below.

### 2.1. *Borohydrides*

Among the borohydrides, the hydrogen content for $LiBH_4$ has reached a value of up to 18 wt.%. $LiBH_4$ can be synthesized by the reaction of ethyl lithium with diborane ($B_2H_6$) [19] or by the direct synthesis from the lithium and boron at 823–973 K in a 3–15 MPa $H_2$ atmosphere [20]. $LiBH_4$ is a hygroscopic crystalline material with a density of 0.66 g $cm^{-3}$ at room temperature [21]. The complex $[BH_4]^-$ anions align along two orthogonal directions and are strongly distorted with respect to bond lengths ($d_{B-H}$ = 1.04(2)–1.28(1) Å) and bond angles ($\angle$H–B–H = 85.1(9)–120.1(9)°) [21,22]. The hydroborate group in the covalent metal hydroborides is bonded to the metal atom by bridging hydrogen atoms similar to the bonding in diborane, which is regarded as the simplest so-called ''electron-deficient'' molecule. Such a molecule possesses fewer electrons than those apparently required to fill all the bonding orbitals, based on the criterion that a normal bonding orbital involving two atoms contains two electrons. Because of these bonding properties, this chemical hydride is stable and temperatures exceeding 673 K are required for the dehydrogenation of pure $LiBH_4$ [21]. This hydride releases three of the four hydrogen atoms that are desorbed at 953 K into a hydrogen atmosphere at pressures up to 10 atm [23]. The dehydrogenation is exothermic, implying that the reverse reaction (hydrogenation) is not thermodynamically favored. Recent efforts have been devoted to incorporating additives, such as metal oxides [21,24], metals [25], hydrides [25–27], metal halides [24,27], sulfides [27], nanoporous scaffolds [27], or lithium amide [28–30] to thermodynamically destabilize the borohydrides toward an optimized (lowered) temperature for hydrogen release. A new quaternary L–B–N–H system, formed by reacting $LiBH_4$ and $LiNH_2$ powders in a 1:2 molar ratio by ball milling or heating above 368 K, releases a large amount of hydrogen (>10 wt.%) below 623 K [29,30]. However, the dehydrogenation temperature is still high for practical application. In addition, the decomposition product had not yet achieved a significant hydrogenation by heating under $H_2$ gas up to 8 MPa while the dehydrogenated product using some other additives, such as $V_2O_5$, $TiO_2$, $TiCl_3$, and $MgH_2$, reversibly adsorbed hydrogen at high temperature (>673 K) and high pressure (>7 MPa) [24,26]. Recently, the correlation between the thermodynamic stability of $M(BH_4)_n$ (M = Li, Na, K, Mg, Ca, Al, Zn, Zr, etc.; $n$ = 1–4) and the electronegativity $\chi_p$ of M has been systematically investigated [31,32], and it was experimentally observed that the dehydrogenation temperature of $M(BH_4)_n$ synthesized by ball milling $MCl_n$ and $LiBH_4$ decreases with increasing the value of $\chi_p$. Well-crystallized $Mg(BH_4)_2$ was synthesized by the metathesis reaction of $MgCl_2$ with $NaBH_4$ in diethyl ether and decomposes to desorb approximately 13.7 wt.% when heated to 800 K [33]. It is still a crucial subject to decrease the dehydrogenation temperature of $M(BH_4)_n$.

An alternative way to generate hydrogen from borohydrides is their reaction with water, so-called hydrolysis [6,7,34–44]. When compared to $LiBH_4$, $NaBH_4$ has been more widely studied because this chemical hydride provides a safe and low-cost practical route to produce hydrogen. $NaBH_4$ can be synthesized by the reaction of sodium trimethyloxyborohydride or sodium tetramethylborohydride with diborane ($B_2H_6$) [45], or by the direct synthesis of sodium, boron, and hydrogen at 823–973 K in a 3–15 MPa $H_2$ atmosphere [20]. $NaBH_4$ is a NaCl-type crystalline material with a density of 1.074 g $cm^{-3}$ [21]. From an X-ray investigation [46], it was mentioned that the sodium and boron atoms may form a body-centered tetragonal array and that the hydrogen atoms could lie on a primitive tetragonal lattice. $NaBH_4$ spontaneously reacts with water [35], while the spontaneous hydrolysis can be depressed in alkaline solutions. The solution can effectively liberate hydrogen at room temperature in the presence of catalysts [6,7,35–44] via the following reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (2\text{-}1)$$

By using 1.5 wt.% Pt–$LiCoO_2$, one of the most active catalyst for this reaction, 4 equiv. of hydrogen can be generated in 16 min (molar ratio: Pt/$NaBH_4$ = 0.0002) [38]. It is reported that the catalytic activities of Pt-based catalysts can be enhanced by decreasing the Pt particle size [38,40]. Besides the Pt-based materials, some non-noble transition elements, such as Co, also exhibit high activities. Hydrogen is released from an aqueous $NaBH_4$ solution in 2.5 min in the presence of a fluorinated cobalt catalyst (molar ratio: Co/$NaBH_4$ = 0.0056) [37]. The effect of the particle size on the catalytic activities of a Co-based catalyst has also been reported [42]. A Co–B thin film can be prepared by a pulsed laser deposition technique, and the obtained Co-based material has a catalytic activity (reaction completed within 100 min with Co/$NaBH_4$ = 0.0299) 2.5 times higher than that of the Co powder catalyst. Hydrogen generation from the hydrolysis of $NaBH_4$ is an excellent choice for a one-time application as the reaction is not reversible and leads to borate waste materials. An effective regeneration process for converting the spent borate back to $NaBH_4$ is required for the successful implementation of this system.

### 2.2. *Ammonia borane*

Ammonia borane, $NH_3BH_3$, contains 19.6 wt.% hydrogen, which is higher than that in $LiBH_4$. $NH_3BH_3$ is synthesized by two methods for laboratory-scale preparation, i.e., salt metathesis and a direct reaction. The combination of ammonium salts with borohydrides (salt metathesis) gives $NH_3BH_3$ in a high

yield [17,47,48]. The direct reaction of ammonia gas with $BH_3$·THF [48], diborane [49], or $BH_3$·$SMe_2$ [50] also affords $NH_3BH_3$ in workable yields. $NH_3BH_3$ is a tetragonal crystal at room temperature, having a staggered conformation with a B–N bond distance of 1.564(6) Å, B–H bond distance of 0.96(3)–1.18(3) Å, and N–H bond distance of 0.96(3)–1.14(2) Å [51]. The solid state structure exhibits short BH···HN intermolecular contacts; the hydridic hydrogen atoms on boron are 2.02 Å away from the protic hydrogen atoms on nitrogen of an adjacent molecule, a distance less than the Van der Waals distance of 2.4 Å, implying an interaction constituting a dihydrogen bond [52,53]. The stability conferred by the dihydrogen bonding (ca. 90.4 kJ $mol^{-1}$) [54] contributes to the existence of $NH_3BH_3$ as a solid under standard conditions. Through a thermal decomposition, 2.2 equiv. of hydrogen can be released from $NH_3BH_3$ up to 473 K [55]. The thermal decomposition temperature of $NH_3BH_3$ can be lowered in an organic solution or ionic liquid [56,57]. Loading $NH_3BH_3$ into a mesoporous silica, SBA-15, can also benefit its thermal decomposition of which the temperature threshold for hydrogen release and the volatile by-products are notably lower than those for neat $NH_3BH_3$ [8]. It was reported that using the nest-like $Ni_{0.88}Pt_{0.12}$ hollow sphere catalyst, $NH_3BH_3$ released 2.2 equiv. of $H_2$ up to 453 K [15]. Metal amidoboranes, such as $LiNH_2BH_3$, derived from the reactions between $NH_3BH_3$ and metal hydrides (such as LiH, NaH [58], or $CaH_2$ [59]) can release up to 11 wt.% hydrogen with a significantly lower emission of borazine by-product. Especially, $LiNH_2BH_3$ and $NaNH_2BH_3$ can release hydrogen below 368 K without a significant borazine emission [58].

In organic solvents, acid-catalyzed [9] or transition metal complex catalyzed [60–62] dehydrogenation can also control hydrogen release to a much wider extent, and hydrogen up to 18 wt.% (>2.5 equiv. of hydrogen) relative to $NH_3BH_3$ is released at 333 K. The Ni–N–heterocyclic carbene (NHC) catalyst system exhibits an unprecedented degree of dehydrogenation to a soluble cross-linked borazine structure [62].

Another option for hydrogen generation from $NH_3BH_3$ is its reaction with water or alcohol, the so-called hydrolysis or alcoholysis. While $NH_3BH_3$ is relatively stable in neutral water and alcohol, the hydrolysis of $NH_3BH_3$ proceeds rapidly in an acidic solution [63,64]. To solve the engineering problem for the intermittent use of hydrogen fuel, employing solid and gaseous acids for the hydrolysis of $NH_3BH_3$ has been proposed [11]. We can also make use of metal catalysts to control the hydrolysis or alcoholysis rates [10,12–15,17]. Hydrogen can be released from the hydrolysis or alcoholysis of $NH_3BH_3$ by the following reactions:

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \quad (2\text{-}2)$$

$$5NH_3BH_3 + 22CH_3OH \rightarrow [NH_4B(OCH_3)_4]_5 \cdot 2CH_3OH + 15H_2 \quad (2\text{-}3)$$

Table 1 summarizes the performance of various catalysts for the hydrolysis of $NH_3BH_3$ [10,12–15]. The reaction rate significantly depends on the metal catalysts or precatalysts employed. Pt-based catalysts show the highest activities, with which reaction (2-2) can be completed within 2 min using Pt/$NH_3BH_3$ = 0.018 [10,13]. TEM observations of the catalysts after reaction indicate that smaller and more dispersed the Pt nanoparticles, higher the catalytic activities. For practical use, low-cost non-noble metal catalysts are desired. As shown in Table 1, supported non-noble metal (Ni or Co) catalysts exhibit high activities, with which hydrogen is released in an almost stoichiometric amount from aqueous $NH_3BH_3$, and the reaction can be completed in 55–70 min [12]. Most importantly, amorphous Fe nanoparticles have recently been found to have an excellent catalytic activity for the hydrolysis of aqueous $NH_3BH_3$ under argon and even in air at room temperature, releasing hydrogen of $H_2/NH_3BH_3$ = 3.0 in ca. 8 min. These high catalytic-active Fe amorphous nanoparticles are synthesized by the in situ $NaBH_4$ reduction of an Fe salt in an aqueous solution of $NH_3BH_3$, which is very simple to handle [14]. No activation process is needed and the Fe catalyst can be easily separated using a magnet after the reaction. Hydrogen generation from $NH_3BH_3$ is kinetically preferable for practical applications, while the efficient and cost effective regeneration of the spent compounds resulting from the dehydrogenation of $NH_3BH_3$ is critical to the successful application of $NH_3BH_3$ as a hydrogen storage system.

Fig. 1 shows a comparison of the hydrogen release from the different boron-based chemical hydrogen storage materials

**Table 1 – Hydrogen generation from aqueous $NH_3BH_3$ catalyzed by noble and non-noble metals.**

| Catalyst | Metal/$NH_3BH_3$ ratio (mol/mol) | Maximum $H_2/NH_3BH_3$ ratio[b] (mol/mol) | Time for reaction completion (min) | Ref. |
|---|---|---|---|---|
| 2 wt.% Ru/γ-$Al_2O_3$ | 0.018 | 3.0 | 3.0 | [10,13] |
| 2 wt.% Rh/γ-$Al_2O_3$ | | 3.0 | 1.3 | |
| [Rh(1,5-COD)(μ-Cl)]$_2$ | | 2.6 | 15.0 | |
| 2 wt.% Pd/γ-$Al_2O_3$ | | 2.9 | 120.0 | |
| Pd black | | 2.6 | 250.0 | |
| 2 wt.% Pt/γ-$Al_2O_3$ | | 3.0 | 0.8 | |
| 2 wt.% Pt/C | | 3.0 | 1.5 | |
| 2 wt.% Pt/$SiO_2$ | | 3.0 | 3.0 | |
| $PtO_2$ | | 3.0 | 8.0 | |
| Pt black | | 3.0 | 12.0 | |
| 2 wt.% Au/γ-$Al_2O_3$ | | 1.9 | 610.0 | |
| 10 wt.% Co/γ-$Al_2O_3$ | 0.018 | 2.9 | 70.0 | [12] |
| 10 wt.% Co/$SiO_2$ | | 2.9 | 70.0 | |
| 10 wt.% Co/C | | 2.9 | 55.0 | |
| 10 wt.% Ni/γ-$Al_2O_3$ | | 2.9 | 65.0 | |
| 10 wt.% Cu/γ-$Al_2O_3$ | | 2.9 | 590.0 | |
| 10 wt.% Fe/γ-$Al_2O_3$ | | –[c] | –[c] | |
| In situ synthesized Fe particle[a] | 0.12 | 3.0 | 8.0 | [14] |
| Ni powder | 0.025 | –[c] | –[c] | [15] |
| Ni hollow sphere | | 0.6 | 120.0 | |
| $Ni_{0.88}Pt_{0.12}$ hollow sphere | 0.020 | 3.0 | 30.0 | |

a Synthesized by the reduction with $NaBH_4$ in the presence of $NH_3BH_3$.
b $H_2/NH_3BH_3$ ratio at the completion of reaction.
c No reaction.

reviewed in this chapter. The released hydrogen is calculated according to the total weight of the chemical hydrogen storage materials plus the weight of the reactants such as $MgH_2$, $LiNH_2$, $H_2O$, etc. It is obvious that the dehydrogenation temperatures of the $LiBH_4$ systems are high, whereas the temperatures of the $NaBH_4$ hydrolysis and the $NH_3BH_3$ thermolysis and hydrolysis are relatively low. It should be noted that some systems include solvents and support/hosts, which should be taken into consideration for calculating their total hydrogen capacities.

## 3. Nitrogen-based chemical hydrogen storage materials

Nitrogen-based chemical hydrogen storage materials, such as the metal–N–H systems, ammonia, and hydrazine, offer excellent potentials for hydrogen storage because of their high hydrogen contents. Several approaches have been suggested for controlling their hydrogen generation rates. Some developments in hydrogen generation from nitrogen-based chemical hydrogen storage materials are reviewed in the next section.

### 3.1. *Metal–N–H systems*

Li–N–H hydrogen storage systems based on lithium amide, $LiNH_2$, have been investigated as early as 1910 [65,66]. It was revealed that $LiNH_2$ was generated along with lithium hydride, LiH, via the following reaction:

$$Li_3N + 2H_2 \rightarrow LiNH_2 + 2LiH \quad (3\text{-}1)$$

It was later revealed that reaction (3-1) consisted of two steps described as reactions (3-2) and (3-3). It was also demonstrated that 6.5 wt.% hydrogen was reversibly desorbed and absorbed at 528 K according to reaction (3-3) [5]:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH \quad (3\text{-}2)$$

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH \quad (3\text{-}3)$$

where $Li_2NH$ is termed as lithium imide. $LiNH_2$ is crystallized in the tetragonal space group $I4$ with the lattice constants of $a = 5.034\ 42(24)$ Å and $c = 10.255\ 58(52)$ Å. Hydrogen atoms occupy the 8g1 (0.2429, 0.1285, 0.1910) and 8g2 (0.3840, 0.3512, 0.1278) sites. The two values of $d_{N-H}$ are 0.986 and 0.942 Å, and the H–N–H bond angle is about 99.97° [67]. This hydrogen storage material has strong ionic characteristics between the ionic $Li^+$ cation and the covalent bonded $[NH_2]^-$ anion. Its valence charge distribution stretches along the direction of the nearest Li neighbor.

Various additives, such as metals, metal salts, or oxides, have been considered to improve the kinetics and reversibility as well as lowering the dehydrogenation temperature via reaction (3-3) [68,69]. The presence of $TiCl_3$ with the ball-milled mixture of $LiNH_2$/LiH (1:1 molar ratio) can effectively lower the dehydrogenation temperature from about 673 K to 573 K along with fast kinetics and a good reversibility [68].

Another way of enhancing the dehydrogenation reaction of $LiNH_2$ (reaction (3-3)) is to partially substitute Li with other elements of higher electronegativity, such as Mg [70]. Charge compensation by the $Li^+$ cation is a major factor in the destabilization of the $[NH_2]^-$ anion, and substitution with a more electronegative element weakens the ionic interaction with this anion. $LiNH_2$ or LiH with partial or complete Mg substitution has been also investigated for the dehydrogenation reaction [71–73]. The mixture of $Mg(NH_2)_2$/LiH can release a large amount of hydrogen at a lower temperature than the mixture of $LiNH_2$/LiH [73–75]; the mixture of $Mg(NH_2)_2$ and LiH at the molar ratio of 3:8 M can generate about 7.0 wt.% hydrogen below 573 K [75].

The metal–N–H systems offer an excellent potential, while further improvements are still required in order to meet practical applications at moderate temperatures. Moreover, ammonia (<0.24% ($NH_3/H_2$)) formed as a reaction by-product of the metal–N–H systems [76,77] should be reduced and/or eliminated in order to avoid poisoning the anode catalysts of the PEM fuel cells [78].

### 3.2. *Ammonia*

Ammonia, $NH_3$, contains 17.7 wt.% hydrogen. $NH_3$ can be synthesized by the Haber–Bosch process, which is one of the

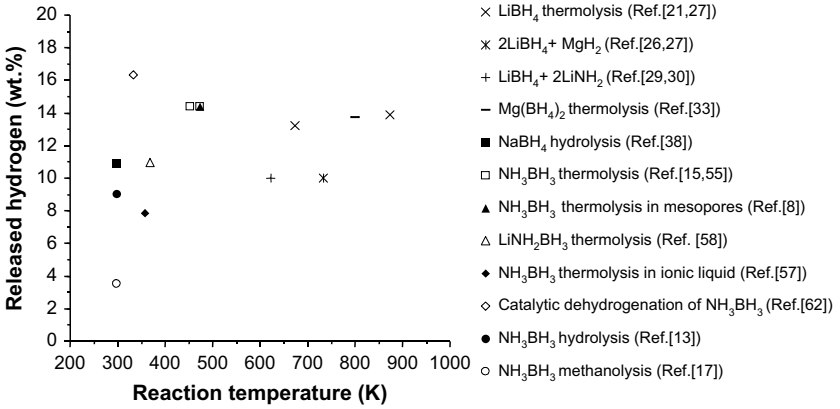


**Fig. 1 – Comparison of the hydrogen release from various boron-based chemical hydrides.**

largest and best studied chemical processes in the world [79,80], and the use of ammonia as an energy storage was proposed around 1980s [81]. All three hydrogen atoms in an ammonia molecule form covalent bonds with the nitrogen in a tetragonal direction. The value of $d_{N-H}$ and the H–N–H bond angle are 1.01 Å and 107°, respectively [82]. This compound is normally encountered as a gas, while it can be liquefied under mild conditions [83]. It can be decomposed to generate hydrogen along with nitrogen by the following reaction:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (3\text{-}4)$$

This reaction is endothermic ($\Delta H = 92$ kJ/mol) and a high temperature is required for efficient hydrogen generation. Various supported catalysts have been found to be effective for ammonia decomposition [84–94], and Ru catalysts are the most active among these catalysts [84,86–93]. The use of porous supports (e.g., carbon nanotubes, mesoporous silica) and an alkali promoter enhances the catalytic activities of the Ru catalysts, and the magnesia–carbon nanotubes supported Ru catalyst modified by $KNO_3$ shows an 80% conversion of $NH_3$ at 673 K [87]. The effects of porous supports on the catalytic activities of Ni catalysts have also been reported [90,94]. However, the decomposition temperatures are still too high for practical use.

Another way to generate hydrogen from $NH_3$ is the combination with metal hydrides [72,74,75,95,96]. 8.1 wt.% Hydrogen from LiH and $NH_3$ can be released at room temperature via the reaction of LiH in an $NH_3$ atmosphere of 0.5 MPa [96] by the following reaction:

$$LiH + NH_3 \leftrightarrow LiNH_2 + H_2 \quad (3\text{-}5)$$

Reaction (3-5) is a reversible reaction, and $LiNH_2$ can store 8.1 wt.% hydrogen at 573 K under a 0.5 MPa hydrogen flow. It is desirable for practical application to lower the hydrogenation temperature.

### 3.3. *Hydrazine*

Hydrazine contains 12.6 wt.% hydrogen. It can be synthesized by the reaction between hydrazinium chloride ($N_2H_5Cl$) and sodium ethoxide ($C_2H_5ONa$) or the reaction between ammonia ($NH_3$) and hypochlorous sodium (NaClO) [97]. Each $H_2N$–N subunit in a hydrazine molecule is in a pyramidal shape. The values of $d_{N-N}$ and $d_{N-H}$ are 1.449 Å and 1.021 Å, respectively. Anhydrous hydrazine is a colorless oily liquid, while it fumes in air [98]. This compound is hypergolic, namely it explosively reacts upon contact with oxidizing agents. However, diluted hydrazine in water or an inert gas is stable, and the decomposition of hydrazine is controllable in the presence of a catalyst. The decomposition reaction occurs around 523 K via the following reaction [18]:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \quad (3\text{-}6)$$

Supported metals [18,99,100], metal nitrides [101,102], or metal carbides [103,104] are active catalysts for the decomposition reaction. Most of the reported catalysts show a high activity for reaction (3-6) at temperatures below 573 K [18,99,101–104]. Hydrogen generation from hydrazine over these catalysts was observed at high temperature due to the further decomposition of $NH_3$ (reaction (3-4)). Interestingly, hydrazine decomposed over supported Ni, Pd, and Pt with the hydrogen selectivities higher than 90% between 303 and 353 K in a fixed bed inert gas diluted flow system [18]. The hydrogen selectivities increase with the reaction temperature in the range of 303–353 K, and then quickly decrease when the reaction temperature is further increased. It is suggested that two competing reactions (3-6) and (3-7) are occurring during the hydrazine decomposition over these supported catalysts.

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad (3\text{-}7)$$

At higher temperature (>673 K), the hydrogen selectivity turns to increase again due to the decomposition of $NH_3$ (reaction (3-4)). The $Ni/SiO_2$ catalyst has been reported to exhibit a high activity. Otherwise, $Ir/Al_2O_3$ exhibits a high activity for the decomposition of hydrazine hydrate to hydrogen at room temperature in a batch system [100]. Over 91% hydrazine hydrate is converted into nitrogen and hydrogen in the presence of the $Ir/Al_2O_3$ catalyst. These two reports indicated that the selection of catalysts is important for hydrogen generation from hydrazine at room temperature.

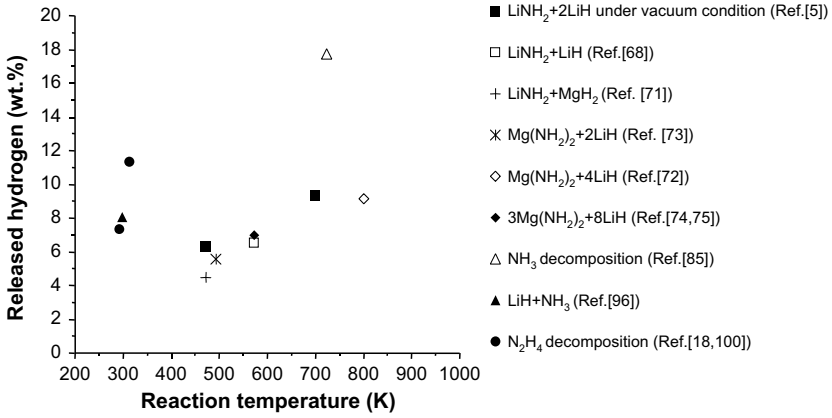


**Fig. 2 – Comparison of the hydrogen release from various nitrogen-based chemical hydrides.**

**Table 2 – Hydrogen generation from various chemical hydrides for fuel cells.**

| Reaction | Hydrogen yield (g $H_2$/g reactant) | Capacity[a] (Wh/g reactant) |
|---|---|---|
| $LiBH_4 + 2LiNH_2 \rightarrow Li_3BN_2 + 4H_2$ | 0.119 | 2.25 |
| $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ | 0.109 | 2.06 |
| $NH_3BH_3 \rightarrow NHBH + 2H_2$ | 0.131 | 2.47 |
| $NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$ | 0.090 | 1.71 |
| $LiNH_2 + LiH \rightarrow Li_2NH + H_2$ | 0.065 | 1.23 |
| $2NH_3 \rightarrow N_2 + 3H_2$ | 0.178 | 3.35 |
| $LiH + NH_3 \rightarrow LiNH_2 + 2H_2$ | 0.081 | 1.52 |
| $N_2H_4 \rightarrow N_2 + 2H_2$ | 0.126 | 2.38 |

a Assuming a standard PEM fuel cell operates at 0.7 V, the generation of 1.0 g $H_2$ $s^{-1}$ corresponds to 96.5 kA × 0.7 = 68 kW.

Three nitrogen-based chemical hydrogen storage materials/systems have been described here. Fig. 2 shows a comparison of the hydrogen release from the nitrogen-based chemical hydrogen storage materials reviewed in this chapter. The released hydrogen is calculated according to the total weight of the chemical hydrogen storage materials plus the weight of reactants, such as LiH and $MgH_2$. When compared to the metal–N–H systems and ammonia, lower dehydrogenation temperatures were observed for the $N_2H_4$ and LiH–$NH_3$ systems.

## 4. Comparison of boron- and nitrogen-based chemical hydrogen storage materials

For comparison of the chemical hydrogen storage materials as potential hydrogen sources, we estimated the power levels using the chemical hydrogen storage materials based on the previously mentioned reactions. Table 2 shows the hydrogen yields and power levels using the chemical hydrogen storage materials by the various reactions. Under appropriate conditions, 0.119, 0.109, 0.131, 0.090, 0.065, 0.178, and 0.126 g of hydrogen are liberated per 1.00 g of the reactants, $LiBH_4 + 2LiNH_2$, $NaBH_4 + 2H_2O$, $NH_3BH_3$, $NH_3BH_3 + 2H_2O$, $LiNH_2 + LiH$, $NH_3$, and $N_2H_4$, respectively. The generation of 1.0 g $H_2$ $s^{-1}$ corresponds to 96.5 kA × 0.7 = 68 kW, assuming that a standard PEM fuel cell operates at 0.7 V [38]. For supplying hydrogen to such a PEMFC system to produce 1 kW of electric power for 1 h, the amounts of the reactants, $LiBH_4 + 2LiNH_2$, $NaBH_4 + 2H_2O$, $NH_3BH_3$, $NH_3BH_3 + 2H_2O$, $LiNH_2 + LiH$, $NH_3$, and $N_2H_4$ need to be 0.44, 0.48, 0.41, 0.59, 0.81, 0.30, and 0.42 kg, respectively.

## 5. Conclusions

Boron- and nitrogen-based chemical hydrogen storage materials, due to their high hydrogen contents, are expected to be potential hydrogen sources for PEM fuel cells. Efforts have been devoted to decrease their dehydrogenation and hydrogenation temperatures and enhance the kinetics. Recently, several approaches have been investigated for hydrogen generation from these compounds at reasonable temperatures and rates, and some of the developments in the hydrogen generation from the boron- and nitrogen-based chemical hydrogen storage materials were reviewed in detail. Some reversible dehydrogenation and hydrogenation systems (e.g., metal–N–H) have exhibited high potentials for hydrogen storage, while their reaction temperatures need to be decreased. Studies of the hydrolysis of $NaBH_4$, the catalytic dehydrogenation of $NH_3BH_3$, the hydrolysis or alcoholysis of $NH_3BH_3$, and the catalytic decomposition of $N_2H_4$ show the possibility of hydrogen generation under mild conditions. For most of the reactions, catalysts play important roles in controlling the reaction kinetics and product selectivity, and effective regeneration processes are required for the successful implementation of the compounds as practical hydrogen storage materials.

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