A review of hydrogen storage systems based on boron and its compounds

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Abstract

This work is a survey of utilization of boron for hydrogen storage. Boron is a promising element for hydrogen storage with its chemical hydrides and nanostructural forms. It is also used as an additive in nickel metal hydride battery systems to enhance hydrogen compatibility and performance. This present study will be a brief summary of hydrogen storage technology in general and focus on possible uses of boron and its compounds.

Contents

1. Introduction

From the beginning of industrialization, humankind has been consuming natural resources without thinking about the environmental impact and possible consequences of their exhaustion. A major effect of using fossil fuels is global warming, which causes hundreds of deaths in warm climate countries, increasing levels of sea water worldwide which threatens seaside cities, and numerous other natural disasters such as floods, hurricanes, forest fires, and so on. At this point we have to think which way to choose: stop the exhaustion of resources, accelerate the transition to renewable energies, or continue consuming fossil fuels and accelerate the world toward a disastrous end. We hope we choose the first option.

Clean energy technologies, namely, solar energy, wind power, hydro power, biomass energy, geothermal energy, tidal energy and wave power technologies are improving very rapidly. The main problem with these technologies is that energy produced from these sources is difficult to store or transport. Significant amounts of electricity are lost while moving long distances on electric power lines. It is obvious that an energy carrier is needed for all of these energy sources, which will be hydrogen, giving its name to the new era coming soon—The Hydrogen Era.

Hydrogen can be produced by numerous techniques, with no emission of pollutants and greenhouse gases at all, and the costs will be competitive as the technology improves [1]. Hydrogen is able to carry energy without any loss for hundreds of kilometers, requiring only a small pumping power. There are a few different approaches for hydrogen transportation and storage. Conventional storage systems consist of classical high-pressure tanks and insulated liquid

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hydrogen systems. Also hydrogen storage in hydrocarbons is a conventional method, but it is out of our scope as it creates carbon dioxide emission. Using metal hydrides in electrochemical batteries is an old and rapidly improving method for hydrogen storage. They are capable of absorbing and desorbing hydrogen with small pressure variations. Utilization of hydrides is also a promising technique for on-board hydrogen storage. A new method is the use of nanostructural materials such as carbon and boron nitride nanotubes, which are known to have the property to store gases within their structure.

The main scope of this paper is to present the possible utilization of boron for hydrogen storage. Various concepts will be introduced here below.

2. Methods of hydrogen storage with boron

Hydrogen storage methods incorporating boron can be divided into four main parts. These are: pyrolysis (decomposition of the substance upon heating to generate hydrogen), hydrolysis (reaction of the substance with water to liberate hydrogen), metal-hydride batteries in which, kinetics are enhanced by boron addition to the electrodes, and boron nitride nanotubes which have the ability to store hydrogen in their framework and liberate it upon heating.

2.1. Pyrolysis of chemical hydrides

Pyrolysis is defined as the decomposition of a substance upon heating. Metal hydrides generate hydrogen gas via reversible pyrolysis reactions, i.e.

$$2M + xH_2 \rightleftharpoons 2MH_x + HEAT, \qquad (1)$$

where M is a metal or an alloy. Such reactions are reversible and hydrogen can be stored by hydriding the metal under high pressure exothermically.

Thermal analysis of alkali metal tetrahydroborides was investigated by Stasinevich et al. [2] and the thermal decomposition is reported to be reversible, at least in early stages. With 18 wt% hydrogen content, $LiBH_4$ was studied by Zuttel et al. [3], three step decomposition and 13.5 wt% hydrogen production was reported. Reversibility was reported to be a failure at 650°C and 150 bar H_2 pressure. The reaction mechanisms and hydrogen storage properties are presented in Tables 1 and 2.

There are numerous other compounds with high hydrogen content which are presented in Table 3 [4].

For comparison, studies on hydrides without boron will be summarized here. Hydriding/dehydriding processes of lithium hydride (LiH), lithium aluminum hydride ($LiAlH_4$) and sodium aluminum hydride ($NaAlH_4$) were studied by several research groups, as these compounds are the most feasible ones for hydrogen storage.

Thermal decomposition processes of $LiAlH_4$, $NaAlH_4$ and some other complex hydrides were studied by Ashby and Kobetz [5] in 1966 and their studies were followed

by Mikhieva and Arkhipov [6] in 1967. In 1971, Ashby and Dilts found similar results for thermal decomposition of $LiAlH_4$ and $NaAlH_4$ [7]. According to this study $LiAlH_4$ decomposed similarly as Mikhieva et al. [6] observed, in three stages at temperatures 154°C, 197°C and 580°C resulting 7.89 wt% H_2. Similarly $NaAlH_4$ was observed to decompose in two steps, 212°C and 250°C to give a H_2 yield of 5.43 wt%. In 1997, Bogdanovic et al. [8] published a paper, reporting that they have accelerated these reactions in both directions. But hydrogenation pressures were still too high (60–150 bar) and conditions should have been improved. A new fabrication technique was introduced in 1999 by Zaluski et al. [9], which was the so-called ball milling technique. $LiAlH_4$ was concluded to be unusable for reversible hydrogen storage as it cannot be re-hydrogenated easily. For $NaAlH_4$, re-hydrogenation took 5 h at 150 atm hydrogen pressure so it was concluded that using complex hydrides for hydrogen storage is feasible. Then Jensen et al. [10] reported a dry doping method of Ti-based catalysts that enhanced the hydrogenation kinetics of sodium alanates. Very recently, Meisner et al. [11] investigated the reversible hydrogen storage kinetics of sodium alanates with Ti and Pt doping. Briefly, sodium alanate is thought to be a potential candidate for hydrogen storage with 200°C desorption temperature and 104°C, 87 atm H_2 for 17 h re-hydrogenation conditions.

Hydrogen production reactions of selected chemical hydrides and some properties of these compounds are presented in Tables 1 and 2. With a 13 wt% H_2, LiH was found to decompose at 825°C and regenerate from Li metal and water at 350°C with a thermodynamic voltage of 0.67 V according to Ref. [46]. $LiAlH_4$ with 10.6 wt% H_2, decomposes in two steps to liberate 8.2 wt% H_2. Two different regeneration mechanisms were presented in Appendix A; one is exactly reverse of pyrolysis, and the other, reaction of LiH and $AlCl_3$ in ether. Two step decomposition reactions of $NaAlH_4$ were presented in Table 1, according to Ref. [10]. Reaction yield H_2 in wt% was found to be 5.55.

Apart from the complex hydrides presented above, there is a class of nitrogen compounds, which produce hydrogen via irreversible thermal decomposition. By the introduction of Hydrogen Economy concept in early 1970s, research on hydrogen storage and carriage with ammonia gained velocity. With 17.6 wt% H_2 content, ammonia was seen as a potential candidate for fuel cell applications. But its extreme toxicity and hazardous effects on health were very important drawbacks for ammonia usage in on-board hydrogen energy systems. So the class of compounds, amine-boranes were begun to be investigated as hydrogen carriers [12–19].

Pyrolysis of ammonia-borane (BH_3NH_3) was studied by Geanangel et al. [20] in 1978 and found that BH_3NH_3 decomposed to BNH and H_2 in two steps at 120°C and 155°C. Decomposition is observed to follow the path:
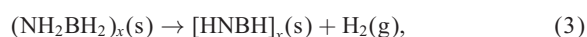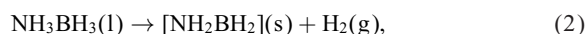
$$NH_3BH_3(l) \rightarrow [NH_2BH_2](s) + H_2(g), \qquad (2)$$

$$(NH_2BH_2)_x(s) \rightarrow [HNBH]_x(s) + H_2(g), \qquad (3)$$

Table 1
Hydrogen production reactions of selected chemical hydrides

Hydride/reaction type	Reaction	Conditions	Ref.
Lithium hydride			
Pyrolysis	$2LiH \rightarrow H_2 + 2Li$	$\Delta H = 132$ kJ/mol H_2 at 825°C	[46]
Regeneration	$2Li + H_2O \rightarrow 2LiH + \frac{1}{2}O_2$	Min. 0.67 V at 350°C	[46]
Magnesium hydride			
Hydrolysis	$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$		[30]
Regeneration	N/A		[30]
Lithium borohydride			
Hydrolysis	$LiBH_4 + H_2O \rightarrow LiOH + H_3BO_3 + 4H_2$		
Regeneration (1)	$3LiH + 4BF_3 \rightarrow BH_3 + 3LiBF_4$		
Regeneration (2)	$LiH + BH_3 \rightarrow LiBH_4$		
Lithium borohydride			
Pyrolysis (1)	$LiBH_4 \rightarrow LiBH_{4-x} + \frac{1}{2}(x)H_2$	at 108°C	[3]
Pyrolysis (2)	$LiBH_{4-x} \rightarrow$ "$LiBH_2$" $+ \frac{1}{2}(1-x)H_2$	at 200°C	[3]
Pyrolysis (3)	"$LiBH_2$" $\rightarrow LiH + B + \frac{1}{2}H_2$	at 453°C	[3]
Lithium aluminum hydride			
Pyrolysis (1)	$LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$	at 160°C	
Pyrolysis (2)	$Li_3AlH_6 \rightarrow 3LiH + Al + \frac{3}{2}H_2$	at 200°C	
Regeneration 1st Method	$Li_3AlH_6 + 2Al + 3H_2 \rightarrow 3LiAlH_4$	> 50 bar H_2	
Regeneration 2nd Method	$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$	at RT, in ether	
Sodium borohydride			
Hydrolysis	$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$	at RT with Ru	[27,28]
Regeneration (1)	$3NaBH(OMe)_3 + 4BF_3 \rightarrow BH_3 + 3NaBF_4 + 3B(OMe)_3$		
Regeneration (2)	$NaBH(OMe)_3 + BH_3 \rightarrow NaBH_4 + B(OMe)_3$		
Sodium aluminum hydride			
Pyrolysis (1)	$3NaAlH_4 \rightarrow Na_3AlH_6 + 3H_2 + 2Al$	at 120°C, Ti doped	[10]
Pyrolysis (2)	$Na_3AlH_6 \rightarrow 3NaH + Al + \frac{3}{2}H_2$	at 250°C	[10]
Regeneration	$NaH + Al + \frac{3}{2}H_2 \rightarrow NaAlH_4$	104 C, 87 atm H_2, 17 h	[10]

Recently, Wolf et al. [21] also studied the thermal decomposition of BH_3NH_3. There are no studies found about the reversibility of this reaction in the literature but preparation of BH_3NH_3 was studied from diammoniate of diborane and lithium borohydride [22,23]. These studies show that if the cost of ammonia-borane production were to be reduced, it would be realized to use it for on-board hydrogen applications such as fuel cells.

2.2. Hydrolysis of chemical hydrides

Hydrolysis is defined as the reaction of a hydride with water to liberate hydrogen gas. The reactions are as follows;

$$MH_x + xH_2O \rightarrow M(OH)_x + xH_2, \qquad (4)$$
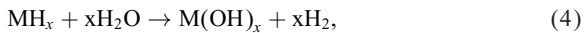
where M is a metal and x is its valence, or,

$$MXH_4 + 4H_2O \rightarrow 4H_2 + MOH + H_3XO_3, \qquad (5)$$

where M is a Group I metal and X is a trivalent element from Group III.

Hydrolysis reactions above are not reversible reactions. However, a very recent study by Kojima et al. [48] describes a concept for converting $NaBO_2$, the hydrolysis product of $NaBH_4$ back to $NaBH_4$ using coke or methane. The reaction of $NaBH_4$ and MgH_2 is represented as follows:

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO. \qquad (6)$$
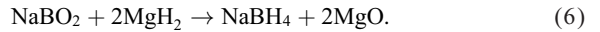
To compare with pyrolysis hydrides, $LiBH_4$ and $NaBH_4$ will be investigated here. These hydrides are of interest for hydrogen storage since Schlesinger et al. [24] published a paper about sodium borohydride for generation of hydrogen in 1952. It was proposed that $NaBH_4$ would be a potential reducing and hydrogen-generating agent as it liberated 2.37 l of H_2/mol of compound at standard conditions and the rate could be increased by increasing the temperature or acidity. Since then, many research groups investigated numerous types of metallo borohydrides and other complex

Table 2
Hydrogen performances of selected chemical hydrides

	LiH	MgH$_2$	LiBH$_4$	LiAlH$_4$	NaBH$_4$	NaAlH$_4$
CAS RN	7580-67-8	60616-74-2	1649-15-8	16853-85-3	1690-66-2	N/A
Formula H$_2$ wt%	13	7.6	18.2	10.6	10.5	7.4
Hydrogen production reaction[a]	Pyrolysis	Hydrolysis	Hydrolysis	Pyrolysis	Hydrolysis	Pyrolysis
Reaction yield H$_2$ wt%	13	∼ 6.2 [47]	13.8 [47]	8.82	10.8 [27,28]	5.55
Absorption conditions	at 825°C, 0.317 bars H$_2$ [46]	20 h ball milling [30]	N/A	at Room Temp. > 50 atm H$_2$ [9]	N/A	at 104°C, 87 atm H$_2$, 17 h [10]
Desorption conditions	at 950°C [46]	4 h for complete hydrolysis [30]	2.5 wt% H$_2$ combined with organics [25]	at 200°C [9]	at Room temperature [27,28]	180–235°C [11]
Density (g/cm^3)	0.78	1.45	0.66	0.917	1.07	N/A
Heat of hydrolysis (kJ/mol H$_2$)	−145	−160	−90	−150	−80	−142

[a] Some chemicals may also produce hydrogen through the other reaction type but reaction which is more feasible was chosen to be presented in this table.

Table 3
Chemical hydrides possible for hydrogen storage [4]

Hydride	wt% H$_2$ (formula)	Availability or synthetic procedure Ref.
Al(BH$_4$)$_3$	16.8	J. Am. Chem. Soc. 75 (1953) 209
LiAlH$_2$(BH$_4$)$_2$	15.2	British Patents 840, 572 and 863,491
Mg(BH$_4$)$_2$	14.8	Inorg. Chem. 11, (1972) 929
Ca(BH$_4$)$_2$	11.5	Synthetic procedure to be developed
Ti(BH$_4$)$_3$	13.0	J. Am. Chem. Soc. 71 (1949) 2488
Zr(BH$_4$)$_3$	8.8	J. Am. Chem. Soc. 71 (1949) 2488
Fe(BH$_4$)$_3$	11.9	Synthetic procedure to be developed

hydrides. Hydrolysis of organics combined LiBH$_4$ and NaBH$_4$ was studied by Aiello et al. [25] in 1998. Results showed that with less violent reactions, these compounds were successful to produce hydrogen. In 1999 Kong et al. [26] investigated the feasibility of hydrogen storage system for alkaline fuel cells using complex hydrides. Although, sodium borohydride and lithium borohydride seemed to be unsuitable for this purpose, Amendola et al. [27,28] and Aiello et al. [29] showed the feasibility of NaBH$_4$ for a portable and safe hydrogen gas generator. Aiello et al. [29] studied LiBH$_4$, NaBH$_4$ and some other hydrides for hydrogen production via hydrolysis with steam, and showed that NaBH$_4$ and LiBH$_4$ have the potential to be utilized as hydrogen storage materials. In fact, NaBH$_4$ has already been commercialized by Millennium Cell as the Hydrogen on Demand[TM] process. Hydrogen is generated in a controllable heat releasing reaction of NaBH$_4$ and H$_2$O at room temperature without high pressure and any side reactions and hazardous by-products. Hydrolysis reactions of some hydrides and hydrogen performances of these are given in Tables 1 and 2. Magnesium hydride was studied by Hout et al. [30] and

reported that it produced hydrogen through hydrolysis reaction with 6.5 wt% yield. With (−160) kJ/mol H$_2$ heat of hydrolysis, MgH$_2$ is the least suitable hydride for hydrogen production in terms of reaction controllability. Reactions of hydrolysis and two-step regeneration are given in appendix for LiBH$_4$, liberating 13.8 wt% H$_2$. In fact, LiBH$_4$ produced 2.5 wt% H$_2$ when combined with organics according to Ref. [25]. Hydrolysis of LiBH$_4$ produces 90 kJ/mol of H$_2$, better than MgH$_2$ but still higher than NaBH$_4$, producing 80 kJ/mol H$_2$. NaBH$_4$, among the other hydrides, seems to be the most feasible compound for hydrogen storage with 10.8 hydrolysis wt% H$_2$, at room temperature. Reactions are given in Table 1 for both hydrolysis and regeneration with different paths, as hydrolysis reaction is not reversible. While producing hydrogen, NaBH$_4$ gives NaBO$_2$ as a by-product, which is used in detergent industry.

To conclude, it would be reasonable to say that boron containing compounds have obvious advantages over the non-containing ones in terms of hydrogen storage performance. Further research should focus on the catalysts for enhanced kinetics, cost reduction of borohydrides and utilization with the introduction of recycling systems for

Table 4
Hydrogen performance improvement of battery electrodes with boron addition

Hydrogen absorbing electrode	Results	Improvement	B Addition wt%	Ref.
$MmNi_{3.2}CoMn_{0.6}Al_{0.2}B_{0.09}$	Discharge capacity increased from 150 to 250 mAh/g at 200 mA/g discharge current	66%	0.211	[31]
$Ti_2Ni_{0.99}(KB)_{0.01}$	Number of cycles increased from 2 to 6 for 300 min at a current density of 20 mA/g	300%	0.065	[32]
$Ti_2Ni_{0.99}(KB)_{0.05}$	Specific capacity increased from 162 to 182 mAh/g at a current density of 20 mAh/g	12%	0.323	[32]
$MmNi_{3.65}Co_{0.62}Mn_{0.36}Al_{0.27}B_{0.1}$	Capacity decay decreased from 24.4% to 16.6% both after 300 cycles	50%	0.0235	[33]
$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}B_{0.3}$	High rate dischargeability increased from 15% to 60% at 3000 mA/g current density	400%	0.707	[35]

by-product borates. Also, research on non-investigated boron hydrides may result in feasible hydrogen containing compounds associated with appropriate catalysts.

2.3. Improvement of battery electrodes with boron

Nickel-based metal hydride batteries began being commercialized by the early 1990s. They offer high hydrogen absorption capacity and reliable absorption/desorption kinetics so that they are favored as power supplies for on-board devices. The whole reaction occurring in the cell is as follows:

$$M + Ni(OH)_2 + H_2O \rightleftharpoons MH + (\beta - NiOOH.H_2O),$$

where M is a metal and forward reaction charges battery while reverse discharges.

Tadokoro et al. [31] investigated the electrochemical characteristics of non-stoichiometric hydrogen absorbing alloys with boron addition. They reported that there was an improvement in discharge rate characteristics probably due to the catalytic effect of the second phase formed by boron. Then in 1995, Luan et al. [32] published a paper about boron and potassium addition to titanium-based electrodes. They concluded that boron was responsible of the specific capacity increase of the electrode. Hu et al. [33] studied rare-earth-based hydrogen storage alloys with small additions of boron in 1998 and they reported that cyclic stability of alloy electrodes increased with small amounts of boron. Ye et al. [34] studied the influence of boron addition on performance of $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ alloy and concluded that boron reduced the hydrogen storage capacity while it simultaneously enhanced the activation performance and high rate capability. Following two studies of Ye et al. [35,36] gave similar results such that boron addition enhanced the performance of hydrogen storage alloys by considerable rates. Quantitative results from these studies were summarized in Table 4.

2.4. Boron nitride nanostructures for hydrogen storage

Carbon nanostructures are a great debate on hydrogen storage issue and research on this field is a very up to date topic. Hydrogen can be stored in carbon nanostructures such as fibers and filaments with varying weight percentages [37–39]. Though, Tibbetts et al. [40] reported a 1 wt% capacity of carbon nanostructures and high temperature and pressure were reported as futile efforts. As an alternative, boron nitride nanostructures can be considered for such application. Wang et al. published a comparison of carbon and boron nitride structures in terms of hydrogen storage capacities and reported that 2.6 wt% H_2 could be stored in an h-BN structure while nanostructured graphite could store up to 7.4 wt% H_2, both after 80 h milling process. BN material, although has disadvantage in capacity, desorbing condition is 30° below than that of the graphite [41]. Oku et al. [42] very recently focused on BN fullerene materials and proposed that BN fullerene would be a good candidate for hydrogen storage applications with its better resistance to heat. Then they also calculated the hydrogen storage capacities of BN fullerenes and concluded that BN stored H_2 easier than carbon fullerenes [43,44]. Ma et al. [45] reported very similar results, such that multiwall BN nanotubes could store up to 2.6 wt% H_2 at room temperature. These results show that BN nanostructures may soon take place of carbon materials for hydrogen storage applications with further research on hydrogen adsorption/desorption mechanism. These results were summarized in Table 5.

3. Conclusion

The importance of boron for hydrogen storage technologies is reviewed. Boron and its compounds are very important for hydrogen economy concept and further research should be carried out in the following fields; cost

Table 5
Boron nitride nanostructures for hydrogen storage

Results	Ref.
2.6 wt% H_2 after 80 h milling, desorption at 570 K	[41]
$B_{36}N_{36}$ hexagonal ring $\Delta E = 14$ eV (14.5% better than C_{60})	[43]
1.8–2.6 wt% H_2 under 10 MPa at room temperature	[45]
BN fullerenes showed possibility of 3 wt% H_2 storage	[46]

reduction and utilization of chemical boron hydrides for hydrogen storage and improvement of hydrogen capacities of boron nanostructures and ammonia–borane complex. Also, using metal hydride batteries, with small amounts of boron addition to the electrodes is a promising field to be further researched.

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