

## Sodium borohydride for the near-future energy: a “rough diamond” for Turkey

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Received: 04.12.2017

Accepted/Published Online: 31.01.2018

Final Version: 27.04.2018

**Abstract:** Boron-based materials are potential solutions in the field of energy. They have been regarded as hydrogen storage materials, liquid fuels of direct liquid-fed fuel cells (DLFCs), electrolytes of battery, and/or energetic substances. A typical example is sodium borohydride ( $\text{NaBH}_4$ ). In sodium hydroxide-stabilized aqueous solutions, it is seen as an efficient  $\text{H}_2$  generator or a performing fuel of DLFCs. Actually, it plays a wider role; it is also the precursor of several boron-based materials of interest in the field of energy. In other words, it is indirectly considered for other energy applications, i.e. solid electrolytes of all solid-state batteries and hypergolic fuel. De facto sodium borohydride has become a key material in the field of energy. This is discussed in the present article, and it is highlighted that sodium borohydride may be clearly seen as a “rough diamond” for Turkey.

**Key words:** Boron-based materials, direct borohydride fuel cell, electrolyte, energy, hydrogen storage, propellant, sodium borohydride

### 1. Introduction

Is there still a need to report the direct causal link of anthropogenic carbon dioxide  $\text{CO}_2$  emissions to global warming? Addressing these critical issues is now urgent and one of the ways is to develop sustainable energies while widening their use.<sup>1</sup> Electricity has an important role but its development faces challenges associated with its storage via technologies like batteries or its generation from fuel cells.<sup>2,3</sup>

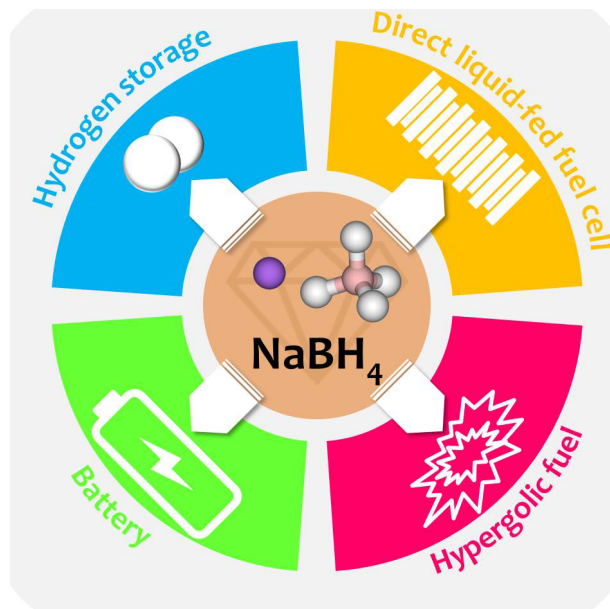
The core principle of an  $\text{H}_2/\text{O}_2$  fuel cell is simple.<sup>3</sup> It is the reverse of electrolysis of water. Fuel cell technology converts the chemical energy stored in  $\text{H}_2$  into electricity. By electrolysis,  $\text{H}_2$  is generated from water and electricity; evolution of  $\text{O}_2$  also takes place but the reaction is thermodynamically unfavorable and requires an important energy input.<sup>4</sup> This then paves the way to alternate H carriers like formic acid  $\text{HCOOH}$ ,<sup>5</sup> ammonia  $\text{NH}_3$ ,<sup>6</sup> liquid organic carriers,<sup>7</sup> and sodium borohydride  $\text{NaBH}_4$ .<sup>8</sup> Research has thus focused on finding appropriate conditions for their catalytic dehydrogenation.

Sodium borohydride was discovered in the 1940s at the University of Chicago under the auspice of the US Army Signal Corps.<sup>9</sup> At that time, new solutions for  $\text{H}_2$  generation in the op-field were sought and  $\text{NaBH}_4$  offered the advantage of generating  $\text{H}_2$  by hydrolysis, that is, by reacting with water at ambient conditions. The reaction was found to be spontaneous and exothermic. It was easily accelerated and even controlled by using a metal-based catalyst.<sup>10</sup> Thereafter and for almost 50 years,  $\text{NaBH}_4$  was little studied in the field of energy.<sup>11</sup> The lean time ended in the 1990s when the company Millennium Cell invested in a  $\text{H}_2$  generation

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prototype based on ruthenium-catalyzed hydrolysis of  $\text{NaBH}_4$ .<sup>12</sup> This was followed by buoyant years, mainly focused on the development of catalysts.<sup>13</sup>

The appeal of  $\text{NaBH}_4$  in the field of energy goes well beyond the aforementioned utilization. On one hand, it has by itself potential in other applications. On the other hand, it is the precursor (i.e. chemical reactant) of various boron-based materials that have been regarded as H carriers, fuels of direct liquid-fed fuel cells, electrolytes of all solid-state batteries, and hypergolic fuels (Figure 1). In other words,  $\text{NaBH}_4$  is a key material for the near-future energy, and this should especially be the case for Turkey.

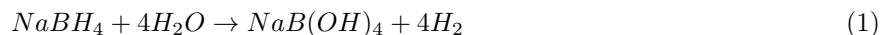


**Figure 1.** Sodium borohydride  $\text{NaBH}_4$ , a key material for four energy applications: hydrogen storage, fuel of direct liquid-fed fuel cells, electrolyte of all solid-state batteries, and hypergolic fuel (i.e. energetic material).

## 2. Energy applications of sodium borohydride and boron-based materials

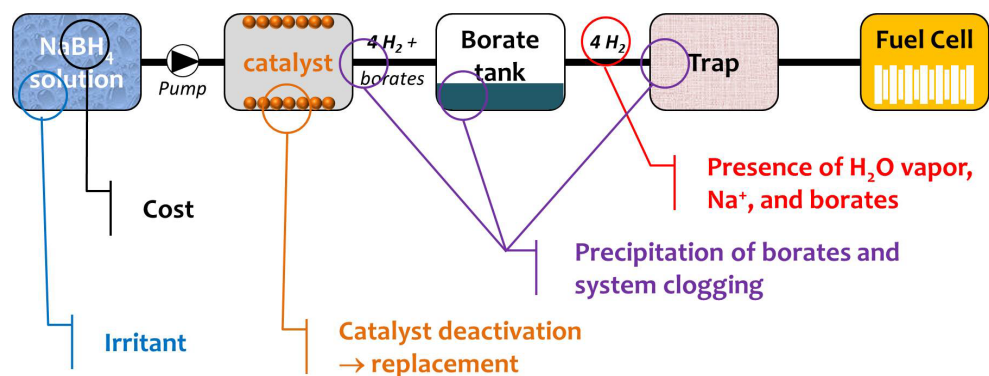
### 2.1. Liquid-state hydrogen storage

Sodium borohydride is soluble in water and is an appropriate hydrolytic (i.e. liquid state) hydrogen storage material.<sup>14</sup> It spontaneously hydrolyzes while liberating  $\text{H}_2$  at slow kinetics:<sup>15</sup>



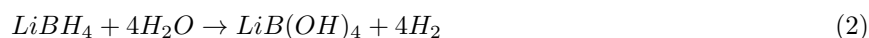
Better stability is achieved by increasing the solution pH beyond 11.<sup>16</sup> Hydrolysis of  $\text{NaBH}_4$  and concomitant  $\text{H}_2$  release can be controlled with the help of a catalyst.<sup>17</sup> The reaction temperature is mostly set between 10 and 40 °C.<sup>13</sup> The by-product is sodium tetrahydroxyborate  $\text{NaB(OH)}_4$ , also soluble in water but to a lesser extent than the borohydride.<sup>18</sup> In the last years, significant advances were made and prototypes and commercial products emerged.<sup>19–21</sup> The reaction today has a high technological readiness level (TRL); it is between TRL7, i.e. “prototype demonstration in a space environment”, and TRL9, i.e. “proven in an operational environment”.<sup>13</sup> However, further development is undermined by important issues. They were reported by Lapeña-Rey et al. (from Boeing R&D Europe, Spain), who worked on a commercial device (200-W<sub>e</sub> fuel cell-powered unmanned

aerial vehicle using an H<sub>2</sub> generator sold by the company Horizon Energy Systems, Singapore).<sup>21</sup> Several critical problems have been identified (Figure 2). The catalyst quickly deactivates, resulting in its indispensable replacement after 8–10 h of operation. The fuel (alkaline aqueous solution of NaBH<sub>4</sub>) is an irritant in nature. The borate by-products precipitate and accumulate in the piping, leading to system clogging. Because of the hydrolysis exothermicity ( $240 \pm 5 \text{ kJ mol}^{-1}$ ),<sup>22</sup> water vapor is generated and then sodium cations and borate anions are carried,<sup>23,24</sup> and thus the released H<sub>2</sub> is polluted. Finally, NaBH<sub>4</sub> is expensive. Lapeña-Rey et al.'s conclusion is, after all, rather positive. They believe in the technology, which would just need some maturation.<sup>21</sup> This is in good agreement with our conclusion from our decade of experience; currently we are working on a prototype that will try to overcome a few of the aforementioned technical problems.



**Figure 2.** Scheme of an example of H<sub>2</sub> generator based on catalytic hydrolysis of NaBH<sub>4</sub>, with focus on five of the issues reported by Lapeña-Rey et al.<sup>21</sup>

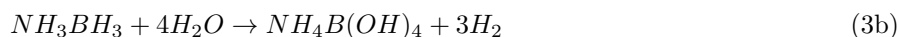
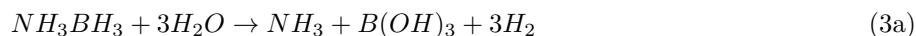
Lithium borohydride LiBH<sub>4</sub> is theoretically more attractive than NaBH<sub>4</sub> owing to an impressive gravimetric hydrogen density of 18.5 wt.% (vs. 10.8 wt.%). Hydrolysis of LiBH<sub>4</sub> has thus been explored:



However, the reaction suffers from several drawbacks. LiBH<sub>4</sub> is much hygroscopic, resulting in instability because of the occurrence of spontaneous hydrolysis.<sup>25</sup> The reaction is incomplete and the mixture of unreacted LiBH<sub>4</sub> and LiB(OH)<sub>4</sub> is difficult to recuperate and handle.<sup>26</sup> The regeneration of LiBH<sub>4</sub> from the anhydrous lithium metaborate LiBO<sub>2</sub> would be impossible.<sup>27</sup> Hence, LiBH<sub>4</sub> has shown to be less attractive than NaBH<sub>4</sub>. Another argument for NaBH<sub>4</sub> is the much higher natural abundance of Na in comparison to that of Li.

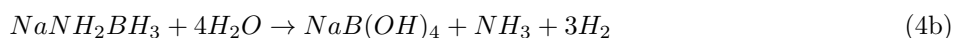
Potassium borohydride KBH<sub>4</sub> was also tested as potential hydrolytic hydrogen storage material.<sup>28</sup> Its properties are similar to those of the sodium counterpart but, because of lower theoretical gravimetric hydrogen storage capacity (7.5 wt.% H), it has been casually considered and little studied.<sup>13</sup>

Ammonia borane NH<sub>3</sub>BH<sub>3</sub> (19.6 wt.% H) is another leading inorganic material in the field of liquid-state chemical H storage.<sup>29,30</sup> It is soluble in water, is stable at pH > 7, and quickly hydrolyzes in the presence of a suitable metal-based catalyst:<sup>31–33</sup>



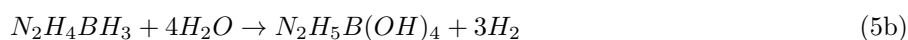
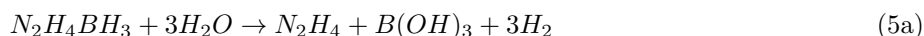
A huge number of metal-based catalysts have been investigated,<sup>34</sup> which in turn resulted in limited studies on the other aspects of the reaction. For example, effective gravimetric hydrogen storage capacity is not optimized yet.<sup>13</sup> No implementable solution has been developed for decreasing, or better yet hindering, the presence of the unwanted  $\text{NH}_3$  in the  $\text{H}_2$  feed.<sup>35</sup> The by-products are of complex composition (more complex than the ideal cases shown by Eq. (3a) and Eq. (3b)); they consist of boric acid  $\text{B}(\text{OH})_3$ , ammonium tetrahydroxyborate  $\text{NH}_4\text{B}(\text{OH})_4$ , and some polyborates,<sup>36</sup> which may make any recycling approach complicated.<sup>37</sup> It is found that hydrolysis of  $\text{NH}_3\text{BH}_3$  is not mature for prototyping yet (TRL4, i.e. “component/breadboard validation at the lab scale”).<sup>13</sup> The main explanation of that lies in fact elsewhere. Above all,  $\text{NH}_3\text{BH}_3$  is a very promising thermolytic hydrogen storage material (cf. Section 2.2).

Two derivatives of  $\text{NH}_3\text{BH}_3$  were also reported as being potential hydrolytic hydrogen storage materials. Lithium amidoborane  $\text{LiNH}_2\text{BH}_3$  (16 wt.% H) and sodium amidoborane  $\text{NaNH}_2\text{BH}_3$  (11.2 wt.% H) were found to spontaneously hydrolyze at 20 °C, liberating  $\text{H}_2$  in less than 30 s:<sup>38</sup>



Unlike for  $\text{NaBH}_4$  and  $\text{NH}_3\text{BH}_3$ , there is no need of a catalyst. This may be seen as an advantage for one-shot applications.

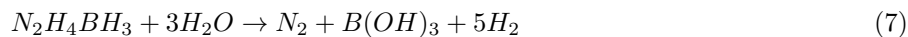
Hydrazine borane  $\text{N}_2\text{H}_4\text{BH}_3$  (15.4 wt.% H) is a derivative of  $\text{NH}_3\text{BH}_3$ . It is soluble in water and, like  $\text{NaBH}_4$  but unlike  $\text{NH}_3\text{BH}_3$ , it slowly hydrolyzes while liberating  $\text{H}_2$ :<sup>39</sup>



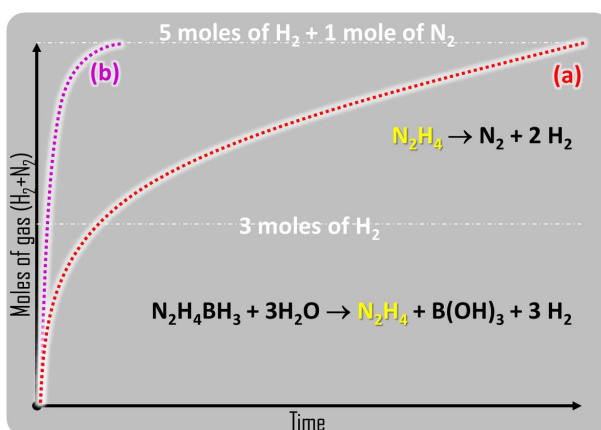
$\text{N}_2\text{H}_4\text{BH}_3$  has a B–N dative bond that is weaker than that of  $\text{NH}_3\text{BH}_3$  and this is the reason why the former is less stable in water and dissociates into the instable hydroxytrihydroborate anion  $\text{BH}_3(\text{OH})^-$ :<sup>40</sup>



Hydrolysis of  $\text{N}_2\text{H}_4\text{BH}_3$  is preferably performed with the help of a metal-based catalyst like rhodium or cobalt.<sup>41,42</sup> Three equivalents of  $\text{H}_2$  are easily recovered with fast kinetics (Eq. (5)). However, the special feature of  $\text{N}_2\text{H}_4\text{BH}_3$  is beyond that. The  $\text{N}_2\text{H}_4$  moiety of  $\text{N}_2\text{H}_4\text{BH}_3$  can be dehydrogenated:<sup>43</sup>



The molecule is then totally dehydrogenated but this requires an effective, active, and selective nickel-based bimetallic catalyst.<sup>43–46</sup> Occurrence of the unwanted decomposition (i.e. a side reaction) of the  $\text{N}_2\text{H}_4$  moiety into  $\text{NH}_3$  is then hindered.<sup>47</sup> Current efforts are dedicated to searching for performing nickel-based bimetallic catalysts in order to smooth the kinetics of  $\text{H}_2$  release (the rates for the hydrolysis of the  $\text{BH}_3$  group and the dehydrogenation of the  $\text{N}_2\text{H}_4$  moiety are different; Figure 3) and improve the catalyst durability/reusability over cycles.<sup>38–47</sup>



**Figure 3.** Schematic representation of the  $5\text{H}_2 + \text{N}_2$  evolution curves for the dehydrogenation of hydrazine borane  $\text{N}_2\text{H}_4\text{BH}_3$  in aqueous medium: (a) stepwise dehydrogenation with the fast hydrolysis of the  $\text{BH}_3$  group followed by the slow dehydrogenation of the  $\text{N}_2\text{H}_4$  moiety; (b) smoothed kinetics with an active and selective catalyst. The second option is expected to occur over cycles.

Recently, a sister compound, hydrazine *bis*borane  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  (16.9 wt.% H), emerged. It is not stable in aqueous media, presumably because of the formation of the instable anion  $\text{BH}_3(\text{OH})^-$ .<sup>40</sup> Hydrolysis takes place to some extent:<sup>48</sup>



The reaction can be catalyzed to accelerate the kinetics. Dehydrogenation via both the  $\text{BH}_3$  and  $\text{N}_2\text{H}_4$  groups takes place, but for an unknown reason the hydrolysis of the  $\text{BH}_3$  group is not total.<sup>49</sup>

Polyboranes have more than one boron atom. The lightest solid-state polyborane is made up of three atoms like the octahydrotriborate anion  $\text{B}_3\text{H}_8^-$ . The first report on hydrolysis of it dates back to 1979.<sup>50</sup> In recent years ammonia triborane  $\text{NH}_3\text{B}_3\text{H}_7$  (17.8 wt.% H) and ammonium octahydrotriborate  $\text{NH}_4\text{B}_3\text{H}_8$  (20.7 wt.% H) were investigated once each.<sup>51,52</sup> Both are able to hydrolyze in the presence of a catalyst. However, the reactions are complex, as evidenced by the heterogeneous composition of the spent fuel with the presence of several species like  $\text{B}(\text{OH})_3$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{B}_3\text{O}_3(\text{OH})_4^-$ ,  $\text{B}_5\text{O}_6(\text{OH})_4^-$ , and so forth. Another drawback is the evolution of  $\text{NH}_3$  together with  $\text{H}_2$ . Heavier polyboranes were also investigated owing to their high stability in aqueous media. Polynuclear anions like *closo*-decaborane  $\text{B}_{10}\text{H}_{10}^{2-}$ , *nido*-undecaborane  $\text{B}_{11}\text{H}_{14}^-$ , and *closo*-dodecaborane  $\text{B}_{12}\text{H}_{12}^{2-}$  were considered,<sup>53,54</sup> but they were finally presented as being less attractive than  $\text{NaBH}_4$  in terms of storage capacity and overall cost.<sup>54</sup> The application prospects for polyboranes are somewhat limited.

In summary, the most advanced and the most suitable boron-based material for liquid-state hydrogen storage is  $\text{NaBH}_4$ . Though not mature yet for wider commercial deployment, it presents fewer technological problems than the other candidates. This is illustrated in the Table.

## 2.2. Solid-state hydrogen storage

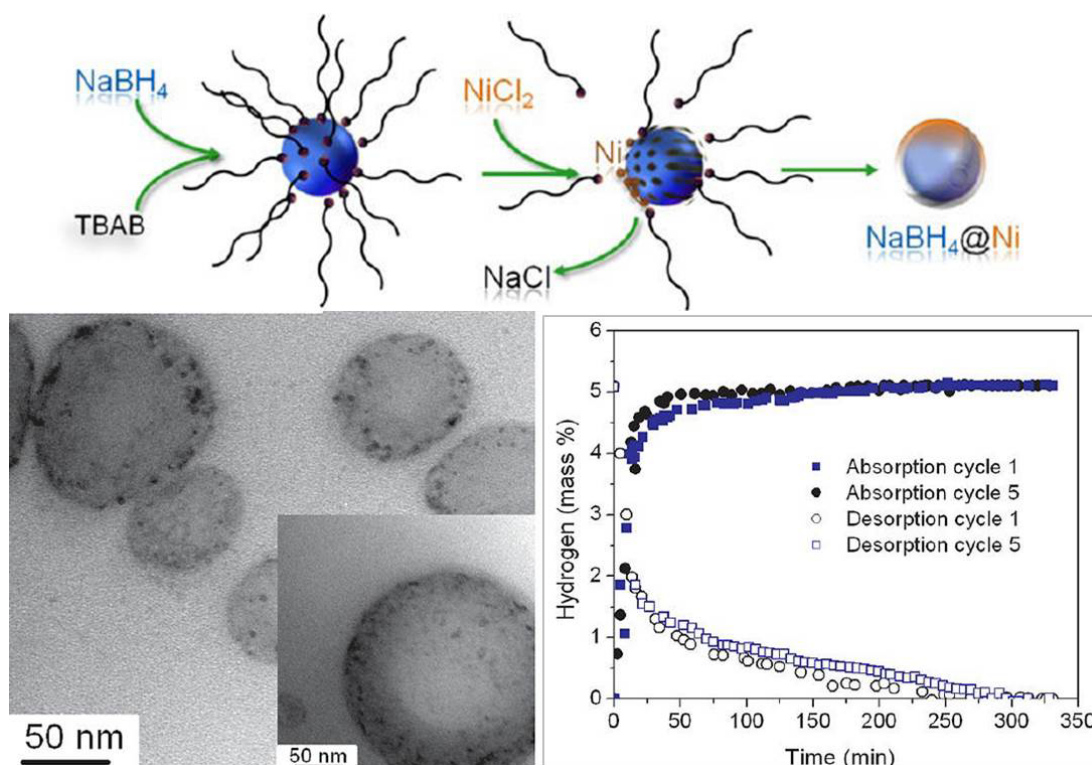
Another attractive feature of most of the boron-based materials is related to their relatively low stability under heating, which makes them potential solid-state hydrogen storage materials (also called thermolytic hydrogen storage materials).<sup>14</sup>

**Table.** Comparison of the various boron-based materials ( $\text{NaBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{KBH}_4$ ,  $\text{NH}_3\text{BH}_3$ ,  $\text{LiNH}_2\text{BH}_3$ ,  $\text{NaNH}_2\text{BH}_3$ ,  $\text{N}_2\text{H}_4\text{BH}_3$ ,  $\text{N}_2\text{H}_4(\text{BH}_3)_2$ ,  $\text{NH}_3\text{B}_3\text{H}_7$ ,  $\text{NH}_4\text{B}_3\text{H}_8$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ) investigated and/or developed for liquid-state hydrogen storage. The comparison is based on the maturity of the technology, the commercial availability of the boron-based material, its cost, the effective gravimetric hydrogen storage capacity (GHSC) in operating conditions, the state of the art of the catalysts, the homogeneous nature of the spent fuel (borate by-products), and the purity of  $\text{H}_2$ . With: +++ for “very favorable”; ++ for “favorable”; + for “could be improved”; no sign for “negative” or if the criterion does not apply.

	Maturity	Avail.	Cost	GHSC	Catalysts	Borates	$\text{H}_2$	Total
$\text{NaBH}_4$	+++	+++	++	+++	+++	+++	+	18+
$\text{LiBH}_4$		+		+	+			3+
$\text{KBH}_4$		+	+		+			3+
$\text{NH}_3\text{BH}_3$	++	+		+	+++	+		11+
$\text{LiNH}_2\text{BH}_3$	+	+		+	+	+		5+
$\text{NaNH}_2\text{BH}_3$	+			+	+	+		4+
$\text{N}_2\text{H}_4\text{BH}_3$	+			+	+	++		5+
$\text{N}_2\text{H}_4(\text{BH}_3)_2$	+			+	+	+		4+
$\text{NH}_3\text{B}_3\text{H}_7$	+			+	+	+		4+
$\text{NH}_4\text{B}_3\text{H}_8$	+			+	+	+		4+
$\text{Na}_2\text{B}_{12}\text{H}_{12}$	+	+		+	+	+	+	6+

Pristine  $\text{NaBH}_4$  dehydrogenates at high temperatures. Martelli et al. found  $534 \pm 10$  °C at 1 bar of  $\text{H}_2$ .<sup>55</sup> Substantial attention has been paid to finding efficient ways to destabilize  $\text{NaBH}_4$  via strategies like catalytic doping (with, e.g., Ti-based additives),<sup>56</sup> nanoengineering (e.g., nanoconfinement into mesoporous matrix, or core@shell nanostructures using nickel as a shell as shown in Figure 4),<sup>57,58</sup> and use of reactive chemicals (i.e. hydrides and fluorides).<sup>59,60</sup> There has been some progress, with improvements being achieved, but lowering a temperature higher than 500 °C to, e.g., 100 °C is a great challenge. The task is even more difficult when highly effective gravimetric hydrogen storage capacities and storage reversibility are simultaneously targeted.<sup>61</sup> The viability of  $\text{NaBH}_4$  as a thermolytic hydrogen storage material depends on the possibility to rehydrogenate as much as possible the thermolytic residue under pressure of  $\text{H}_2$ . Another promising and efficient way to destabilize  $\text{NaBH}_4$  is chemical modification leading to derivatives and in the past decade a wide variety of compounds have been discovered accordingly by developing three approaches.<sup>61,62</sup>

A first approach combines protic hydrogen elements  $\text{H}^{\delta+}$  with the hydridic hydrogen elements  $\text{H}^{\delta-}$  of  $\text{NaBH}_4$ . Sources of  $\text{H}^{\delta+}$  are, e.g., sodium amide  $\text{NaNH}_2$ ,<sup>63</sup> magnesium hydroxide  $\text{Mg}(\text{OH})_2$ ,<sup>64</sup> hydrazine  $\text{N}_2\text{H}_4$ ,<sup>65</sup> and  $\text{NH}_3\text{BH}_3$ .<sup>66</sup> The presence of  $\text{H}^{\delta+}$  improves the thermal properties of  $\text{NaBH}_4$ . For example,  $\text{NaNH}_2$ - $\text{NaBH}_4$  (molar ratios 1:1 and 2:1) has lowered onset temperatures of dehydrogenation (ca. 290 and <400 °C, respectively) thanks to favorable  $\text{H}^{\delta+} \dots \text{H}^{\delta-}$  reactivity,<sup>63,67,68</sup> even though the process exothermicity introduces important challenges in terms of rehydrogenation.<sup>61</sup> A second approach is to substitute  $\text{Na}^+$  by another cation. More than 30 alternate cations have been considered so far.<sup>62</sup> The lightest is  $\text{Li}^+$ ,<sup>69</sup> and among the heaviest one may cite  $\text{U}^{4+}$ .<sup>70</sup> The most investigated borohydrides are mainly  $\text{LiBH}_4$  (18.5 wt.% H),<sup>71</sup> magnesium borohydride  $\text{Mg}(\text{BH}_4)_2$  (14.9 wt.% H),<sup>72</sup> and calcium borohydride  $\text{Ca}(\text{BH}_4)_2$  (11.6 wt.% H).<sup>73</sup>  $\text{LiBH}_4$  releases  $\text{H}_2$  from ca. 268 °C but most of the generation takes place above ca. 380 °C. A total of 13.9 wt.% H can then be released.<sup>74</sup>



**Figure 4.** The top scheme illustrates the chemical process for synthesizing the nanosized core@shell  $\text{NaBH}_4@Ni$  particles (with TBAB as tetra-*n*-butylammonium bromide). At left is shown a TEM image of  $\text{NaBH}_4@Ni$ . The curves at right show the kinetics of  $\text{H}_2$  desorption (0.01 MPa) and  $\text{H}_2$  adsorption (4 MPa) for  $\text{NaBH}_4@Ni$  at 350 °C and for a first and a fifth cycle. Reprinted and adapted with permission from ref. 58. Copyright (2012) American Chemical Society.



The reaction is exothermic, which means unfavorable rehydrogenation properties (limited reversibility).<sup>75</sup>  $\text{Mg}(\text{BH}_4)_2$  is attractive owing to a lower decomposition temperature and more favorable enthalpy of dehydrogenation than those of  $\text{NaBH}_4$  and  $\text{LiBH}_4$ .<sup>72</sup> The enthalpy of dehydrogenation of  $\text{Ca}(\text{BH}_4)_2$  is less exothermic and substantial rehydrogenation (ca. 3.8 wt.% H) was reported (kinetically accelerated by an additive such as  $\text{TiCl}_3$ ).<sup>76</sup> Each of these borohydrides have shown attractive features for chemical H storage but improvements (i.e. lowered dehydrogenation temperature, faster kinetics, and reversibility) are still required. Destabilization by catalytic doping, nanoengineering, use of reactive hydrides, and chemical modification have been investigated.<sup>14,61,62,77</sup> A first example is  $\text{LiBH}_4$  confined into a mesoporous carbonaceous nanoscaffold. The composite is able to release  $\text{H}_2$  from 150 °C and to rehydrogenate at 200 °C and 60 bars of  $\text{H}_2$ .<sup>78</sup> A second example is the complexation of  $\text{Mg}(\text{BH}_4)_2$  with  $\text{NH}_3$  such as  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ . The compound carries 16 wt.% H and starts to decompose at 150 °C according to an endothermic process.<sup>79</sup> There is a third approach that consists of using two or three cations. This is a way to tailor the thermodynamic properties of the borohydride compounds.<sup>61</sup> More than fifty bi-/tri-metallic borohydrides (based on Li, Na, K, Rb, and Cs) were recently surveyed.<sup>62</sup> For example, with Na, the following bimetallic compounds were synthesized:  $\text{NaK}(\text{BH}_4)_2$ ,<sup>80</sup>  $\text{NaSc}(\text{BH}_4)_4$ ,<sup>81</sup>  $\text{NaY}(\text{BH}_4)_4$ ,<sup>82</sup>  $\text{NaLa}(\text{BH}_4)_4$ ,<sup>83</sup>  $\text{NaYb}(\text{BH}_4)_4$ ,<sup>84</sup> and  $\text{NaZn}(\text{BH}_4)_3$ .<sup>85</sup> Nanoconfinement of such bimetallic compounds was also considered.<sup>86</sup>

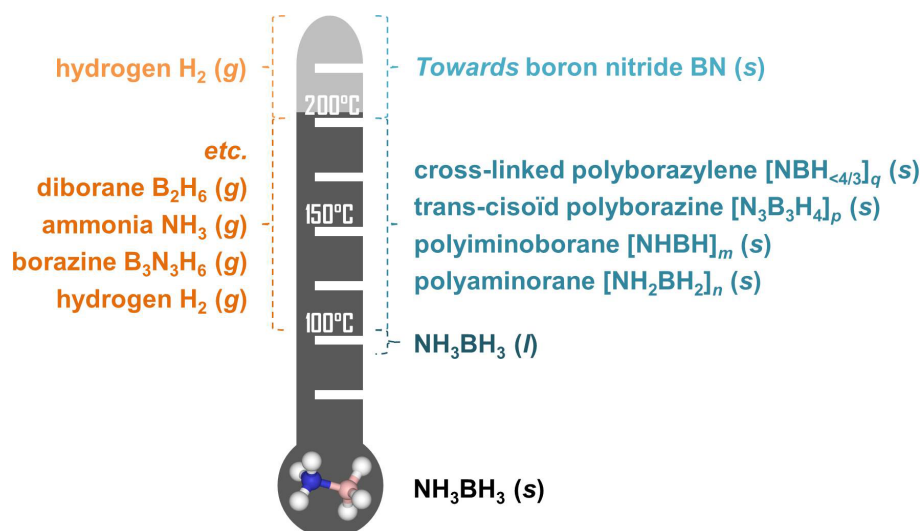
Despite significant improvements in terms of kinetics, storage capacities, and reversibility, none of the borohydrides reported so far have shown to be suitable for implementation and practical application.<sup>61,62</sup> Further progress could be made and  $\text{NaBH}_4$  will certainly play a major role in that. According to Mao and Gregory, the practical solution for chemical H storage may be a material in which sodium borohydride is a component part.<sup>61</sup>

Ammonia borane carries three protic hydrogen elements  $\text{H}^{\delta+}$  together with three hydridic hydrogen elements  $\text{H}^{\delta-}$  that put the  $\text{NH}_3\text{BH}_3$  molecules into heteropolar interactions *via*  $\text{H}^{\delta+} \cdots \text{H}^{\delta-}$  bonds.<sup>87</sup> Such intra- and intermolecular interactions account for the solid state of the compound at ambient conditions and are at the origin of the favorable dehydrogenation properties of the pristine borane since it is able to initiate  $\text{H}_2$  release at around 100 °C.<sup>88</sup> Owing to these properties,  $\text{NH}_3\text{BH}_3$  has been considered as being promising for chemical H storage.<sup>89</sup> However,  $\text{NH}_3\text{BH}_3$  is not suitable if taken in the pristine state (Figure 5). Upon melting (ca. 100 °C), it decomposes into  $\text{H}_2$  and unwanted gaseous by-products like  $\text{NH}_3$  and borazine  $\text{B}_3\text{N}_3\text{H}_6$ . The decomposition is stepwise. The second step occurs at around 150 °C and roughly half of the starting borane is released in the form of various gaseous products (including  $\text{H}_2$ ).<sup>90</sup> A polymeric residue of complex composition forms.<sup>91</sup> Total dehydrogenation takes place at temperatures much higher than 200 °C, resulting in the formation of a highly stable ceramic, i.e. boron nitride BN.<sup>92</sup> The exothermicity of the decomposition clearly compromises any storage reversibility.<sup>93</sup> The only option to close the  $\text{H}_2$  cycle with  $\text{NH}_3\text{BH}_3$  is to recycle the polymeric residue.<sup>94</sup> Great efforts have been focused on strategies for improving the dehydrogenation properties of  $\text{NH}_3\text{BH}_3$ .<sup>95</sup> The main objective is to destabilize the borane for decreasing the onset temperature of dehydrogenation, but it is associated to other subobjectives relating to the purity of the released  $\text{H}_2$  and the formation of a single polymeric residue (i.e. polyborazylene). Four different strategies have been studied: chemical doping by addition of a dopant like ammonium chloride  $\text{NH}_4\text{Cl}$  or copper chloride  $\text{CuCl}_2$ ;<sup>96,97</sup> dissolution in a solvent (e.g., glyme, ionic liquid)<sup>98,99</sup> with or without the addition of a metal-based homogeneous catalyst;<sup>100</sup> nanosizing via nanoconfinement in a porous host material (e.g., silica aerogel and metal organic framework);<sup>101,102</sup> and chemical modification towards derivatives like sodium amidoborane  $\text{NaNH}_2\text{BH}_3$ .<sup>103</sup> For example, attractive performance was reported for nanoconfinement (Figure 6). The first work was reported by Gutowska et al., who successfully destabilized  $\text{NH}_3\text{BH}_3$  after infiltration into mesoporous silica SBA-15.<sup>104</sup> Gao et al. used an amino-modified metal organic framework ( $\text{NH}_2$ -MIL(Cr)-101) to scaffold  $\text{NH}_3\text{BH}_3$ .<sup>101</sup> Nanoconfined  $\text{NH}_3\text{BH}_3$  then released  $\text{H}_2$  from 68.8 °C (with traces of impurities) and up to 1.6 mol of  $\text{H}_2$  per mole of  $\text{NH}_3\text{BH}_3$  evolved at 85 °C.

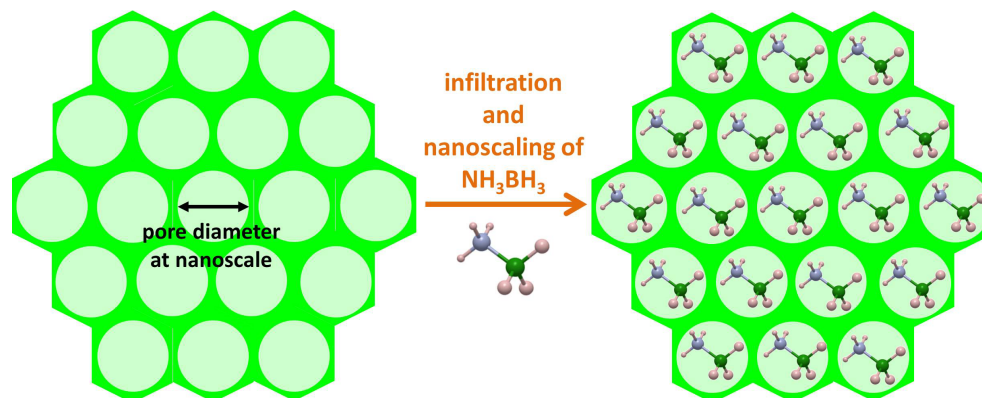
Hydrazine borane  $\text{N}_2\text{H}_4\text{BH}_3$  and hydrazine *bis*borane  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  are both, in the pristine state, unsuitable for solid-state chemical H storage. Under heating, the former generates a high amount of  $\text{N}_2\text{H}_4$  as well as a shock-sensitive residue. The latter is instable (and explodes) at a high heating rate and at temperatures higher than 150 °C.<sup>48,105,106</sup> However,  $\text{N}_2\text{H}_4\text{BH}_3$  cannot be totally discarded as it can be chemically modified to generate alkali derivatives (lithium hydrazinidoborane  $\text{LiN}_2\text{H}_3\text{BH}_3$ , sodium hydrazinidoborane  $\text{NaN}_2\text{H}_3\text{BH}_3$ , and potassium hydrazinidoborane  $\text{KN}_2\text{H}_3\text{BH}_3$ ).<sup>43</sup> The second of these listed derivatives is, for example, able to generate significant amounts of pure  $\text{H}_2$  when doped with 5 wt.% of NaH and heated up to 100 °C.<sup>107</sup>

The most mature of the solid-state/thermolytic hydrogen storage materials is  $\text{NH}_3\text{BH}_3$  owing to favorable properties but also a huge amount of work. It is mature enough for scaling-up and prototyping. For instance, Nam and co-workers developed a  $\text{NH}_3\text{BH}_3$ -based  $\text{H}_2$  generator that is able to feed a 200 W<sub>e</sub> polymer





**Figure 5.** Schematic representation of the stepwise decomposition of ammonia borane  $\text{NH}_3\text{BH}_3$  from 100 to  $>200$  °C. At left are listed the gaseous products that form and at right are shown the different polymeric species that can be identified as parts of the polymeric residue recovered upon heating up to 200 °C.

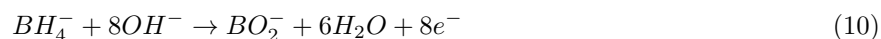


**Figure 6.** Illustration of nanoconfinement of ammonia borane  $\text{NH}_3\text{BH}_3$  into the nanoporosity of a host material (like mesoporous silica). In doing so, nanoscaled grains of  $\text{NH}_3\text{BH}_3$  are obtained.

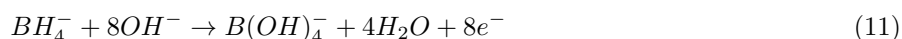
electrolyte membrane fuel cell powering an unmanned aerial vehicle.<sup>108,109</sup> Thermolysis of  $\text{NH}_3\text{BH}_3$  has today a technological readiness level of at least TRL7, i.e. “prototype demonstration in a space environment”.

### 2.3. Direct liquid-fed fuel cells

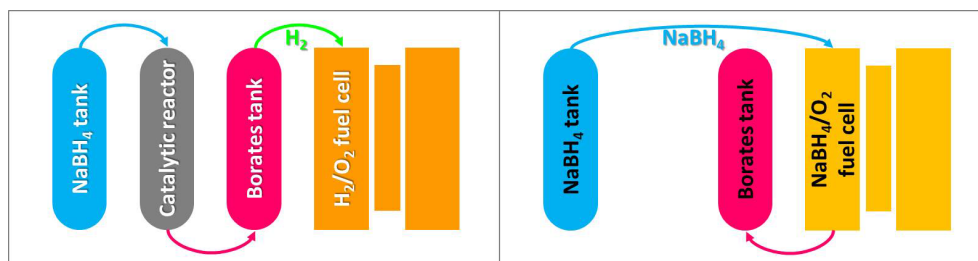
Sodium borohydride is a common selective reducing agent, widely used in organic chemistry.<sup>110</sup> It can be oxidized and the first study about the direct oxidation of the borohydride anion dates back to the 1950s:<sup>111</sup>



Given the thermodynamics of  $\text{BO}_2^-$ , it is unlikely to be stable in aqueous solution at ambient conditions.<sup>112</sup> The following reaction is thermodynamically more suitable:



The standard electromotive force  $E^\circ$  was calculated to be  $-1.24$  V versus the standard hydrogen electrode.<sup>113</sup> In recent years, oxidation of  $\text{BH}_4^-$  has been much investigated with two main objectives: (i) better understanding the fundamentals of the reaction and (ii) finding suitable (active and selective) electrooxidation catalysts.<sup>114</sup> An underlying objective is to find the most optimized experimental and catalytic conditions to oxidize the  $\text{BH}_4^-$  anion while strictly avoiding the unwanted heterogeneous hydrolysis (Eq. (1)).<sup>115–117</sup> For example, gold was found to be a potential electrode owing to high electrocatalytic activity towards oxidation and among the lowest activities towards hydrolysis.<sup>118</sup> It is able to favor the involvement of almost 8 electrons (Eq. (12)), but the oxidation process is irreversible because of the formation of the overly stable borates. Oxidation of  $\text{NaBH}_4$  has also been transferred into fuel cell technology. There is a difference to note between  $\text{NaBH}_4$  as an  $\text{H}_2$  generator for an  $\text{H}_2/\text{O}_2$  fuel cell and  $\text{NaBH}_4$  as a direct fuel of a direct liquid-fed fuel cell (Figure 7). In the former case, the hydrolysis generates  $\text{H}_2$  and the fuel cell is based on the oxidation of  $\text{H}_2$ .<sup>119</sup> In the latter case,  $\text{NaBH}_4$  is in an alkaline ( $\text{pH} > 12$ ) aqueous solution (anodic fuel) and is fed into a direct borohydride fuel cell to be directly oxidized.<sup>120</sup> The direct borohydride fuel cell technology uses the oxidation of  $\text{NaBH}_4$  at the anode (Eq. 12) and generally the reduction of  $\text{O}_2$  at the cathode:<sup>121</sup>



**Figure 7.** Schematic representation of (left) an  $\text{H}_2/\text{O}_2$  fuel cell fed by  $\text{H}_2$  generated by hydrolysis of  $\text{NaBH}_4$  and (right) a direct borohydride fuel cell (i.e.  $\text{NaBH}_4/\text{O}_2$  fuel cell).

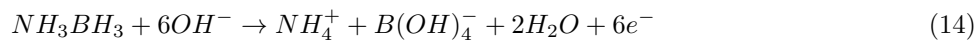


The standard electromotive force  $E^\circ$  of this reaction is  $0.40$  V versus the standard hydrogen electrode. The overall cell reaction is then:

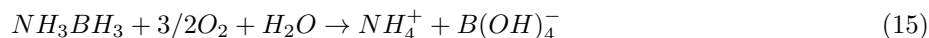


The theoretical cell voltage is  $1.64$  V. This is a voltage that is higher than the theoretical values of the  $\text{H}_2/\text{O}_2$  fuel cell and of the different direct liquid-fed fuel cells reported so far.<sup>122</sup> It is worth mentioning the use of  $\text{H}_2\text{O}_2$  instead of  $\text{O}_2$  as a cathodic fuel.<sup>123</sup> There have been a great number of articles about the oxidation of  $\text{NaBH}_4$  and the direct borohydride fuel cell.<sup>114</sup> Special attention has been paid to the anodic electrocatalyst, the membrane, and the unwanted heterogeneous hydrolysis reaction. These are the main challenging aspects hindering the development of the fuel cell. Indeed, the anodic electrocatalyst is expected to be inactive towards hydrolysis while oxidizing the  $\text{BH}_4^-$  anion at low potentials.<sup>124</sup> The membrane is expected to inhibit the crossover of the  $\text{BH}_4^-$  anions from the anodic compartment to the cathodic one.<sup>125</sup> The heterogeneous hydrolysis has been investigated to better understand the mechanisms and to find ways to avoid its occurrence in the presence of the most suitable electrocatalyst.<sup>126</sup> It is important to avoid its occurrence because no hydrolyzing  $\text{BH}_4^-$  anion is available for oxidation anymore. Timely reviews reported the main achievements and advances over the past decade.<sup>114,122,127–130</sup>

Like for the hydrolysis field,  $\text{NH}_3\text{BH}_3$  has been proposed as a possible alternative to  $\text{NaBH}_4$  for the direct liquid-fed fuel cell technology.<sup>131</sup>  $\text{NH}_3\text{BH}_3$  is stable in alkaline conditions<sup>132</sup> and can be readily oxidized:<sup>133</sup>

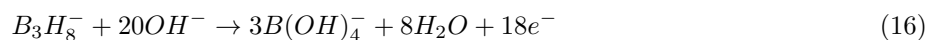


The standard electromotive force  $E^\circ$  was calculated as  $-1.22$  V versus the standard hydrogen electrode.<sup>133</sup> With  $\text{O}_2$  as an oxidant (Eq. (13)), the overall cell reaction is:



The theoretical cell voltage is 1.62 V. The direct ammonia borane fuel cell has been much less investigated in comparison to the direct borohydride fuel cell. There are three reasons: both technologies suffer from the same issues (occurrence of heterogeneous hydrolysis, fuel crossover, and degraded cell efficiency); oxidation of  $\text{BH}_4^-$  theoretically involves more electrons (Eq. (12) versus Eq. (15));  $\text{NH}_3\text{BH}_3$  is more expensive as it is synthesized from  $\text{NaBH}_4$ .<sup>134</sup>

Polyboranes have been considered in this field. There is notably one work on the oxidation of  $\text{B}_3\text{H}_8^-$ :<sup>135</sup>



Bulk platinum and gold electrodes were used to investigate the oxidation reaction. Effective numbers of electrons of 5.2 and 10.1 were found, respectively (out of a theoretical total of 18 electrons). Complete oxidation was not achieved because of the occurrence of heterogeneous hydrolysis as well as the stability of the B–B bond of the  $\text{B}_3\text{H}_8^-$  anion. Another polyborane is sodium dodecahydro-*closo*dodecaborate  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ .<sup>136</sup> It was selected because it is highly stable in aqueous solution. Partial oxidative degradation was observed with platinum, gold, and silver electrodes. The complexity of the process resulted in the formation of several products like the anions  $\text{B}_{11}\text{H}_{11}\text{O}(\text{OH})^-$ ,  $\text{B}_7\text{H}_{11}\text{O}^-$ , and  $\text{B}_7\text{H}_8\text{O}^-$ . Polyboranes are attractive owing to the theoretical high number of electrons involved but, in comparison to  $\text{NaBH}_4$ , they are not competitive enough. The potential of  $\text{NaBH}_4$  will remain better unless an alternate boron-based hydride is able to oxidize into products that can be reversibly reduced (oxidation-reduction cycles vs. oxidation-regeneration cycles for  $\text{NaBH}_4$ ,  $\text{NH}_3\text{BH}_3$ ,  $\text{NaB}_3\text{H}_8$ , and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ).

#### 2.4. Electrolytes of batteries

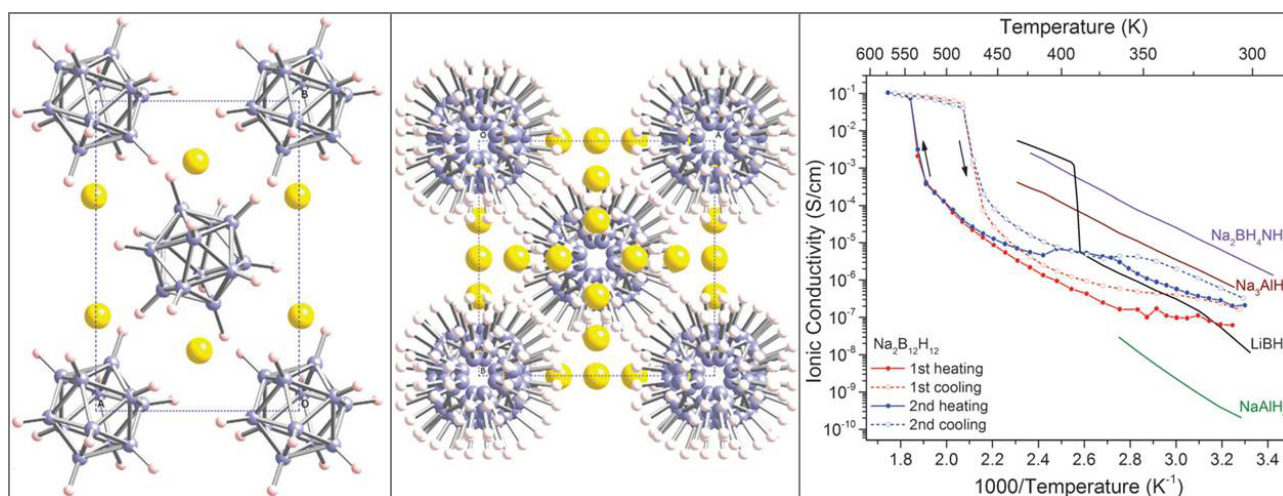
In the recent years, some boron-based compounds appeared to be potential electrolytic materials. Solid electrolytes are of high interest for the development of all solid-state batteries where, e.g., the anode is metallic Li or Na.<sup>137</sup> The prerequisites for a solid electrolyte are as follows: chemical stability, electrochemical stability, negligible electronic conduction, and high Li or Na conductivity ( $\geq 1$  mS  $\text{cm}^{-1}$ ).<sup>138,139</sup>

One of the potential Li-ion conductors was found to be the hexagonal  $P63/mmc$  phase of lithium borohydride  $h\text{-LiBH}_4$ . It has a ionic conductivity of  $2 \times 10^{-3}$  S  $\text{cm}^{-1}$  above 110 °C.<sup>140</sup> Modification of  $\text{LiBH}_4$  has been considered to improve the conductivity. One of the strategies is nanoconfinement into the nanopores of ordered mesoporous silica. A conductivity of  $1 - 10^{-4}$  mS  $\text{cm}^{-1}$  was measured at room temperature, which is a value about three orders of magnitude larger than that of bulk  $\text{LiBH}_4$ .<sup>141</sup> Another strategy is to explore the synthesis of derivatives by substitution of a fraction of  $\text{BH}_4^-$  by larger halide anions (e.g.,  $\text{I}^-$ ),<sup>142</sup> adding a second cation and a chloride (i.e. mixed-cation mixed-anion borohydride chlorides like

$\text{LiCe}(\text{BH}_4)_3\text{Cl}$ ),<sup>143</sup> or mixing a second anion resulting in species like  $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$ .<sup>144</sup> For example, with this last derivative, a conductivity of up to  $2 \times 10^{-4} \text{ S cm}^{-1}$  was measured at room temperature. In a recent report, the lithium amide-borohydride compound with formula  $\text{Li}(\text{BH}_4)_{1/3}(\text{NH}_2)_{2/3}$  showed a conductivity of  $6.4 \times 10^{-3} \text{ S cm}^{-1}$  at  $40^\circ \text{C}$ ; then, for a  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  half-cell using  $\text{Li}(\text{BH}_4)_{1/3}(\text{NH}_2)_{2/3}$  as the electrolyte, a good rate performance up to  $3.5 \text{ mA cm}^{-2}$  ( $5 \text{ C}$ ) was measured at the same temperature.<sup>145</sup> A number of other derivatives could be further developed.<sup>62</sup>

A derivative of  $\text{NaBH}_4$  can be mentioned. A compound similar to  $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$  was developed: Li was replaced by Na to get  $\text{Na}_2(\text{BH}_4)(\text{NH}_2)$ .<sup>146</sup> The Na-ion conductivity was found to be  $2 - 10^{-6} \text{ S cm}^{-1}$  at room temperature.

Polyboranes have high chemical stability and are suitable for ion conduction.  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  is an interesting Na-ion conductor. The disordered cubic phase appearing at  $256^\circ \text{C}$  has a conductivity of  $0.1 \text{ S cm}^{-1}$  (Figure 8).<sup>147</sup> The emergence of the polyboranes opened new prospects for the borohydrides. The  $\text{B}_{12}\text{H}_{12}^{2-}$  and  $\text{BH}_4^-$  anions were, for example, mixed to get Li or Na conductors. The compound  $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$  was, for example, synthesized by solid-solid reaction of  $\text{NaBH}_4$  and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  at  $365^\circ \text{C}$  and was found to have Na-ion conductivity of  $5 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature.<sup>148</sup> Another attractive polyborane is  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ , which as a high temperature polymorph ( $90^\circ \text{C}$ ) has a superionic conductivity of  $1 \times 10^{-2} \text{ S cm}^{-1}$ .<sup>149</sup>



**Figure 8.** Unit cells of (left) the low-temperature ordered monoclinic and (middle) the high temperature disordered cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  structures viewed along the  $c$ -axes. Yellow, purple, and white spheres represent Na, B, and H, respectively. (right) Temperature dependence of the ionic conductivity of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  compared with that for  $\text{NaAlH}_4$ ,  $\text{Na}_3\text{AlH}_6$ ,  $\text{Na}_2\text{BH}_4\text{NH}_2$ , and  $\text{LiBH}_4$ . Reproduced from ref. 147 with permission from the Royal Society of Chemistry.

The present one is clearly a new field. There is room for improvements and better performance could be reported soon, which should open new horizons for boron-based materials.

## 2.5. Hypergolic fuels

In propulsion (requiring energetic materials), a hypergolic fuel (reducer) is able to self-ignite when put into contact with an oxidizer at room temperature.<sup>150</sup> The fuel and the oxidizer are the propellant pair. Typical hypergolic fuels are hydrazine and methylated derivatives. The common oxidizers are white fuming nitric

acid  $\text{HNO}_3$ , dinitrogen tetroxide  $\text{N}_2\text{O}_4$ , and hydrogen peroxide  $\text{H}_2\text{O}_2$ .<sup>151</sup> New fuels have been searched for within the past decade. According to Zhang and Shreeve, boron chemistry is a new opportunity for liquid-state hypergolic propellants.<sup>151</sup> The potential of boron-based materials as propellants, but in solid state, was in fact highlighted in the 1960–1980s. Examples are  $\text{NH}_3\text{BH}_3$ ,  $\text{N}_2\text{H}_4(\text{BH}_3)_2$ , and even a polyborane of formula  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ .<sup>152–154</sup> One may even state that hydrogen storage materials are potential propellants.<sup>150</sup> Two examples are  $\text{NaBH}_4$  and  $\text{KBH}_4$ .<sup>155</sup>

The solubility of borohydride salts in ionic liquids opened new prospects for liquid-state propellants.  $\text{NaBH}_4$  was successfully used to get a borohydride-ionic liquid called trihexyltetradecyl-phosphonium borohydride  $[\text{P}(\text{C}_6\text{H}_{13})_3(\text{C}_{14}\text{H}_{29})][\text{BH}_4]$ , which was thereafter used to form another borohydride-ionic liquid such as  $[\text{P}(\text{C}_6\text{H}_{13})_3(\text{C}_{14}\text{H}_{29})][\text{Al}(\text{BH}_4)_4]$ . The latter was found to be reactive with  $\text{H}_2\text{O}_2$  and an ignition delay time of  $<30$  ms was measured for a drop test.<sup>156</sup> To synthesize other borohydride-ionic liquids, e.g., 1-allyl-3-methylimidazolium borohydride  $[\text{C}_3\text{H}_5(\text{C}_3\text{N}_2\text{H}_3)\text{CH}_3][\text{BH}_4]$  and 1-butyl-3-methylimidazolium borohydride  $[\text{C}_4\text{H}_9(\text{C}_3\text{N}_2\text{H}_3)\text{CH}_3][\text{BH}_4]$ ,  $\text{NaBH}_4$  was systematically used as precursor.<sup>157,158</sup> Drop tests with  $\text{HNO}_3$  revealed ignition delay time of 2 ms for the former liquid.<sup>157</sup>

Ionic liquid-solubilized boranes were also scrutinized as possible hypergolic fuels.  $\text{NH}_3\text{BH}_3$ ,  $\text{N}_2\text{H}_4\text{BH}_3$ , and  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  were dissolved in different ionic liquids and reacted with  $\text{HNO}_3$ .<sup>159</sup> Drop tests showed ignition delay times of 3 to 5 ms for  $\text{NH}_3\text{BH}_3$  and  $\text{N}_2\text{H}_4\text{BH}_3$  in 1-butyl-3-methylimidazolium dicyanamide and 1-butyl-1-methyl pyrrolidinium dicyanamide (Figure 9). With  $\text{N}_2\text{H}_4(\text{BH}_3)_2$ , the ignition delay times were of 31–34 ms. Other amine-boranes (e.g., triethylamine-borane  $\text{N}(\text{CH}_3)_3\text{BH}_3$ , propylamine-borane  $\text{NH}_2(\text{C}_3\text{H}_7)\text{BH}_3$ ) were also considered as borane-ionic liquids.<sup>157,160</sup>

Polyboranes are also potential hypergolic fuels owing to suitable thermal and hydrolytic stability. Jiao et al. studied ionic liquids based on the anions  $\text{B}_6\text{H}_7^-$ ,  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$ .<sup>161</sup> The first two ones showed high hypergolic activities with  $\text{N}_2\text{O}_4$  as an oxidizer. Ignition delay times as short as 1 ms were measured.

Propulsion for spacecrafts or rocketry is a niche application. Boron-based materials could have some prospects in a field that is of strategic importance for countries.

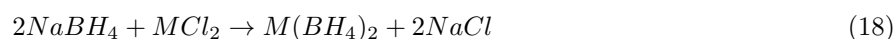
### 3. Discussion

#### 3.1. Sodium borohydride, a key chemical precursor

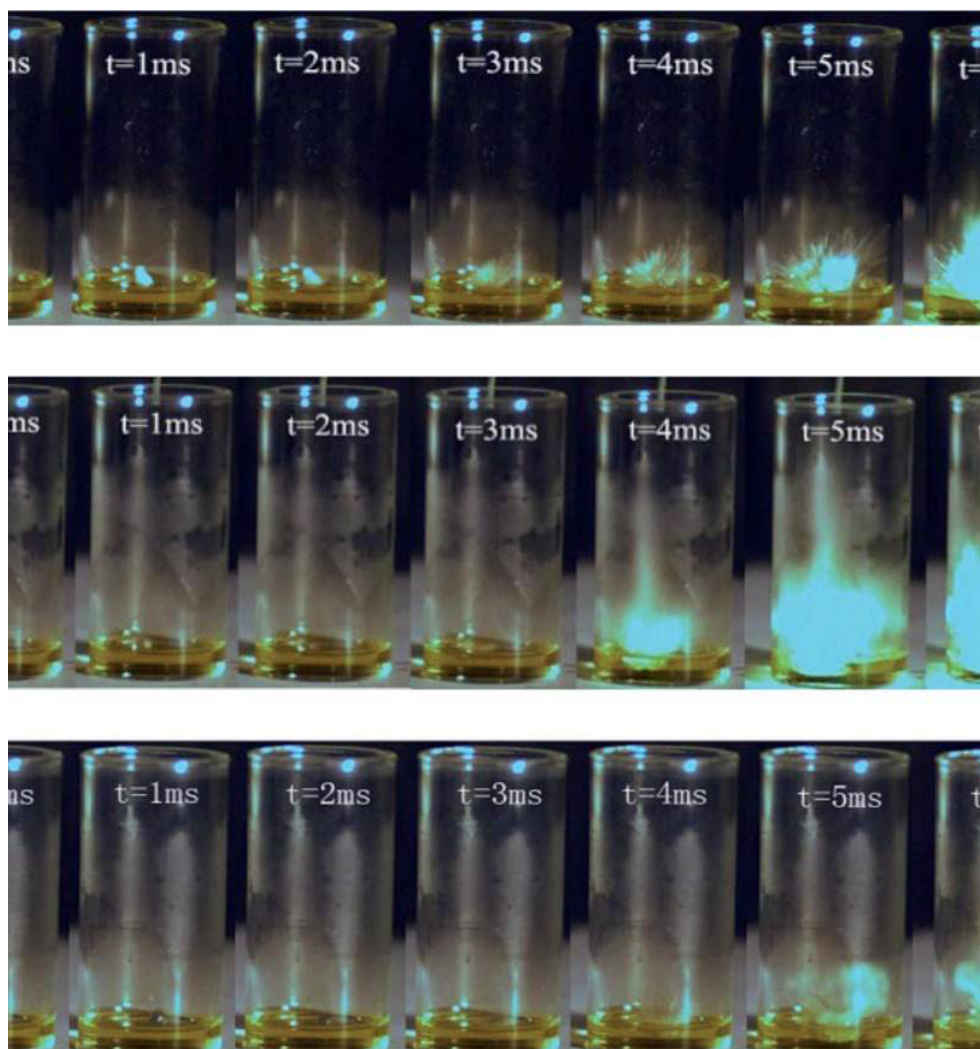
The title of this section is explicit.  $\text{NaBH}_4$  is the key precursor of a number of boron-based materials. Most of the borohydrides can be synthesized from  $\text{NaBH}_4$ . The first example is  $\text{LiBH}_4$ . It can be conveniently prepared at room conditions by metathesis, which means the reaction of  $\text{NaBH}_4$  with a metal halide  $\text{LiX}$  with  $\text{X} = \text{Cl}$  or  $\text{Br}$ :<sup>10,162</sup>



In a similar way, potassium borohydride can be obtained from  $\text{NaBH}_4$ .<sup>163</sup> Two other examples are  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Ca}(\text{BH}_4)_2$  (using  $\text{MX}_2$  such  $\text{M} = \text{Mg}$  or  $\text{Ca}$  and  $\text{X} = \text{Cl}$  or  $\text{Br}$ ):<sup>164,165</sup>



Given that  $\text{NaBH}_4$  may be the precursor of other borohydride salts, it is reasonable to state that it can be at the origin of a wide variety of multimetallic borohydrides (e.g.,  $\text{NaK}(\text{BH}_4)_2$ ,<sup>80</sup>  $\text{NaSc}(\text{BH}_4)_4$ ,<sup>81</sup>  $\text{NaY}(\text{BH}_4)_4$ ,<sup>82</sup>  $\text{NaLa}(\text{BH}_4)_4$ ,<sup>83</sup>  $\text{NaYb}(\text{BH}_4)_4$ ,<sup>84</sup> and  $\text{NaZn}(\text{BH}_4)_3$ <sup>85</sup>).

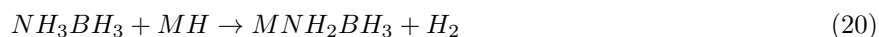


**Figure 9.** Ignition delay tests for hypergolic fuels contacting white fuming  $\text{HNO}_3$  and: (top)  $\text{N}_2\text{H}_4\text{BH}_3$ ; (middle)  $\text{N}_2\text{H}_4\text{BH}_3$  in 1-butyl-3-methylimidazolium dicyanamide; (bottom)  $\text{N}_2\text{H}_4\text{BH}_3$  in 1-butyl-1-methyl pyrrolidinium dicyanamide. Reproduced from ref. 159 with permission from the Royal Society of Chemistry.

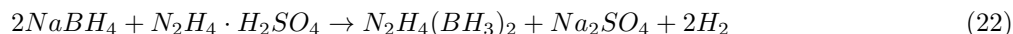
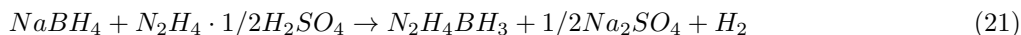
The importance of  $\text{NaBH}_4$  in the advent of  $\text{NH}_3\text{BH}_3$  is primarily related to the synthesis process of the latter. There are various synthetic approaches,<sup>166</sup> but the simplest, most convenient, and widespread route involves  $\text{NaBH}_4$ .<sup>35</sup> A typical example of synthesis is the reaction of  $\text{NaBH}_4$  with an ammonium salt (e.g.,  $\text{NH}_4\text{Cl}$ ) in a suitable organic solvent like tetrahydrofuran:<sup>167</sup>



The reaction is performed at 40 °C for 2 h. A yield of about 80% is generally obtained.<sup>166,167</sup> There are other paths for synthesizing the borane but they are less safe and less easy because of the use of the toxic diborane  $\text{B}_2\text{H}_6$  and of the corrosive ammonia  $\text{NH}_3$ .<sup>168</sup> From  $\text{NH}_3\text{BH}_3$ , alkali derivatives (e.g.,  $\text{LiNH}_2\text{BH}_3$  and  $\text{NaNH}_2\text{BH}_3$ ) can be obtained by solid-state reaction with the alkali hydride  $\text{MH}$  ( $\text{M} = \text{Li}$  or  $\text{Na}$ ):<sup>169</sup>

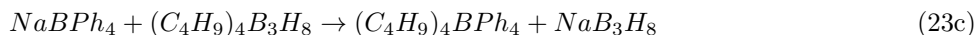
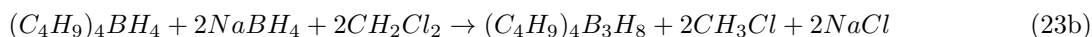
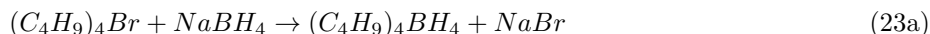


Like  $\text{NH}_3\text{BH}_3$ ,  $\text{N}_2\text{H}_4\text{BH}_3$  and  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  are conveniently synthesized from  $\text{NaBH}_4$ :<sup>48,105,170,171</sup>



Like for the amidoborane derivatives (Eq. (21)), hydrazinidoborane derivatives can be readily or spontaneously obtained by ball-milling or by simply mixing  $\text{N}_2\text{H}_4\text{BH}_3$  with MH (M = Li, Na and K).<sup>43</sup> In other words, a compound like  $\text{NaN}_2\text{H}_3\text{BH}_3$  is obtained from  $\text{NaBH}_4$  through a two-step process.

The octahydrotriborate anion  $\text{B}_3\text{H}_8^-$  can be synthesized from  $\text{BH}_4^-$  by oxidation.<sup>172</sup> For instance, Moury et al. recently proposed a new pathway where  $\text{NaBH}_4$  is transformed (finally oxidized) into  $\text{NaB}_3\text{H}_8$  through a three-step process:<sup>173</sup>



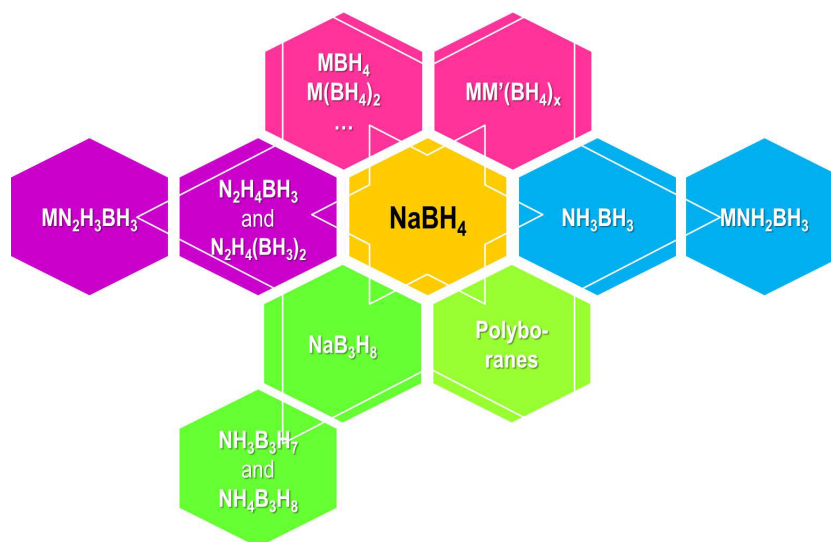
It is interesting to note that in turn  $\text{B}_3\text{H}_8^-$  serves as precursor for the synthesis of  $\text{NH}_3\text{B}_3\text{H}_7$ .<sup>51</sup> This is also the case for  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  that can be obtained by solvothermal decomposition of  $\text{NaB}_3\text{H}_8$ .<sup>136,173</sup> In fact, there are different methods for synthesizing such polyborane. Many of them are based on the oxidation of  $\text{NaBH}_4$  (or another alkali borohydride like  $\text{LiBH}_4$ ).<sup>174</sup> An example of such a path uses  $\text{I}_2$  as oxidizer.<sup>136</sup>

For many years now we have worked on boron-based materials for chemical H storage and direct liquid-fueled fuel cells. We have notably focused on  $\text{NaBH}_4$ ,<sup>13</sup>  $\text{NH}_3\text{BH}_3$  and  $\text{NaNH}_2\text{BH}_3$ ,<sup>95</sup>  $\text{N}_2\text{H}_4\text{BH}_3$  and its Li and Na derivatives,<sup>39,43</sup>  $\text{N}_2\text{H}_4(\text{BH}_3)_2$ ,<sup>48</sup>  $\text{NaB}_3\text{H}_8$ ,<sup>135</sup> and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ .<sup>136</sup> There are other examples, which we will soon communicate. A recent one is lithium hydrazinidoborane ammoniate  $\text{LiN}_2\text{H}_3\text{BH}_3 \cdot 0.25\text{NH}_3$ , a derivative of  $\text{N}_2\text{H}_4\text{BH}_3$  that we found to be a potential  $\text{NH}_3$  carrier rather than a hydrogen carrier.<sup>175</sup> We use to synthesize all of these compounds, directly or indirectly, from  $\text{NaBH}_4$ , and we also used to consider  $\text{NaBH}_4$  at first as a precursor of any new targeted boron-based material. In other words,  $\text{NaBH}_4$  is a key precursor for synthesizing boron-based materials (Figure 10).

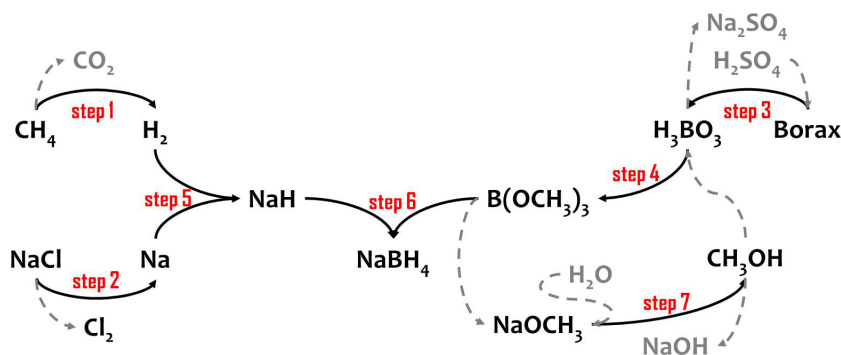
### 3.2. About the synthesis paths of sodium borohydride

A “classical” path for synthesizing  $\text{NaBH}_4$  is the Brown–Schlesinger process (Figure 11). This is one of the current industrial production methods.<sup>10,176</sup> The process is based on the reaction (step 6) of NaH and trimethoxyborate  $\text{B}(\text{OCH}_3)_3$  at  $>200$  °C. In preliminary steps, steam reforming of methane  $\text{CH}_4$  generates  $\text{H}_2$  (step 1) and sodium chloride  $\text{NaCl}$  is electrolyzed to form metallic sodium Na (step 2). The as-obtained  $\text{H}_2$  and Na are reacted in step 5 to form NaH. With respect to  $\text{B}(\text{OCH}_3)_3$ , it is a product of the borax mineral  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and methanol  $\text{CH}_3\text{OH}$  (steps 3 and 4). There is another “classical” path for synthesizing  $\text{NaBH}_4$  at the industrial scale. This is the Bayer process:<sup>177,178</sup>





**Figure 10.** Sodium borohydride  $\text{NaBH}_4$ , a key chemical precursor allowing the synthesizing of a number of boron-based materials like monometallic borohydrides, mixed-metal borohydrides, ammonia borane and derivatives, hydrazine borane and derivatives, hydrazine bisborane, and B3- and B12-polyboranes.



**Figure 11.** The Brown–Schlesinger process<sup>10,176</sup> for the stepwise industrial production of  $\text{NaBH}_4$  from methane as hydrogen source, sodium chloride as metallic sodium source, and borax and methanol as sources of trimethoxyborate.

The borosilicate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 7\text{SiO}_2$  is first obtained by fusion of borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and silica  $\text{SiO}_2$ . It is then reacted with Na under  $\text{H}_2$  pressure at 400–500 °C. This results in the formation of  $\text{NaBH}_4$ , which is finally extracted with liquid  $\text{NH}_3$ .

There are alternative methods for synthesizing  $\text{NaBH}_4$ . They emerged with the advent of  $\text{NaBH}_4$  as a hydrolytic  $\text{H}_2$  generator and fuel of direct borohydride fuel cells. Efforts have been dedicated to finding cost-efficient processes for regenerating  $\text{NaBH}_4$  from the by-product  $\text{NaB}(\text{OH})_4$  (also denoted  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ ) or from the anhydrous form  $\text{NaBO}_2$  (sodium metaborate).<sup>37,176</sup> This is discussed hereafter.

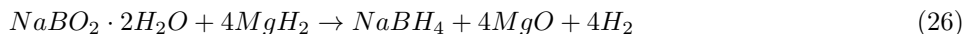
The cheap magnesium hydride  $\text{MgH}_2$  can be used for reforming B–H bonds. Li et al. ball-milled, at room temperature, a solid mixture of  $\text{MgH}_2$ ,  $\text{Na}_2\text{B}_4\text{O}_7$  and sodium carbonate  $\text{Na}_2\text{CO}_3$  as a source of additional Na:<sup>179</sup>



Kojima et al. used  $\text{NaBO}_2$  instead of  $\text{Na}_2\text{B}_4\text{O}_7$ .<sup>180</sup>  $\text{MgH}_2$  and  $\text{NaBO}_2$  were reacted for 2 h at 550 °C under



70 bars of  $H_2$  to generate  $NaBH_4$ . A yield of almost 100% was reported. Improvements with the objective to decrease the overall cost were thereafter achieved. Ball-milling under argon atmosphere,<sup>181</sup> use of Mg (instead of  $MgH_2$ ) in the presence of Si,<sup>180</sup> and use of  $Mg_3La$  hydrides,<sup>182</sup> among others, resulted in better performance. In other works, Mg was substituted by, e.g., Al, Si or Ti.<sup>183,184</sup> To reduce the recycling cost, it is preferable to use the hydrated form of the by-product, i.e.  $NaBO_2 \cdot 2H_2O$ , which is in fact directly recovered upon the hydrolysis or oxidation of  $NaBH_4$ . Note that  $NaBO_2$  forms at 350 °C from the hydrated counterpart.<sup>185</sup> Chen et al. showed that  $NaBO_2 \cdot 2H_2O$  is able to react with  $MgH_2$  via ball-milling:<sup>186</sup>



A yield of almost 90% was achieved. Recycling mediated by a metallic reducing agent like Mg or  $MgH_2$  is the most developed approach to date.<sup>37,176</sup> However, two other approaches may be described. The first one was investigated by Kemmitt and Gainsford.<sup>187</sup> It uses sodium tetramethoxyborate  $NaB(OCH_3)_4$  prepared by alkoxylation of  $NaBO_2$  by methanol. To regenerate  $NaBH_4$  (yield: >80%),  $NaB(OCH_3)_4$  is refluxed in diglyme solvent with sodium alanate  $NaAlH_4$ :



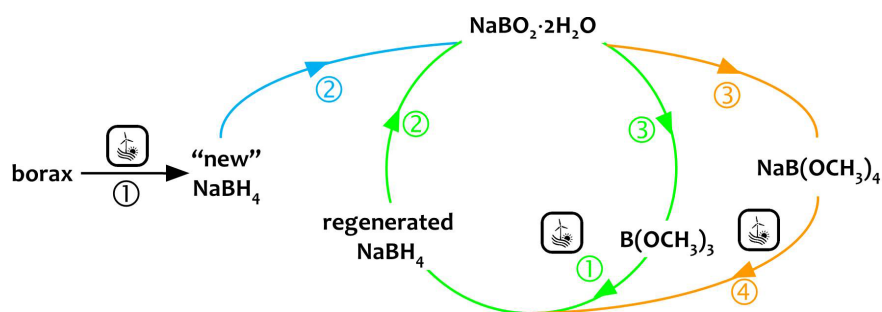
The viability of this reaction is compromised as  $NaAlH_4$  is very expensive to produce. However, there is room for improvement with this reaction provided that a cheaper hydride source is developed. The second approach is based on electrosynthesis, namely the reverse of the reaction shown by Eq. (12).<sup>188</sup> The standard electromotive force  $E^\circ$  is 1.24 V versus the standard hydrogen electrode. This is a high energy-demanding process.<sup>189</sup>

Hydrolyses of  $NH_3BH_3$  and  $N_2H_4BH_3$  lead to the formation of  $B(OH)_3$  in equilibrium with  $B(OH)_4^-$  (Eq. (3) and Eq. (5)). At pH levels tending to acidic values, the compound  $B(OH)_3$  predominates;<sup>190</sup> otherwise, any excess of  $B(OH)_4^-$  can be transformed into  $B(OH)_3$  in acidic medium.<sup>191</sup> Following an approach similar to that reported by Kemmitt and Gainsford,<sup>187</sup>  $B(OH)_3$  may be alkoxyated by methanol to form  $B(OCH_3)_3$ , which is one of the key reactants of the Brown–Schlesinger process (Figure 11).<sup>10,176</sup> To be viable, such a regeneration approach must take into consideration recovery and recycling of  $NH_3/NH_4^+$ , another by-product of hydrolysis of  $NH_3BH_3$ . With  $N_2H_4BH_3$ , complete dehydrogenation (Eq. (7)) should lead to  $N_2$  as the other by-product and then should avoid any recycling of N-containing by-product.

The recycling processes suffer from needs of a lot of energy (heat or electric power).<sup>176</sup> They are dependent on what the energy costs. The B–O is as energetic as the C–O bond of carbon dioxide  $CO_2$ , which gives an idea of the energy constraints. Liu and Chen, on the one hand,<sup>176</sup> and Monteverde and Magistri, on the other hand,<sup>192</sup> emphasized that the only solution is the use of electricity from renewable sources like wind power and solar power (among other options). A cost of 19 \$  $kg^{-1}$  for  $NaBH_4$  instead of 236 \$  $kg^{-1}$  (in 2011) was even calculated.  $NaBH_4$  would then be competitive. The aforementioned achievements suggest that further efforts could help in making  $NaBH_4$  viable and implementable in the field of energy (Figure 12).

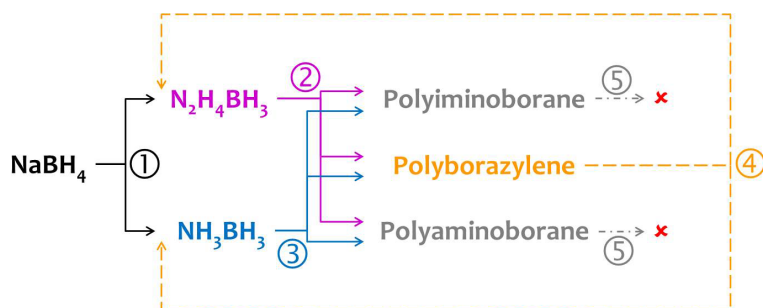
### 3.3. Regeneration of the other boron-based materials

For borohydrides considered as solid-state hydrogen storage materials, one of the targeted properties for implementation is reversibility of  $H_2$  storage. In other words, rehydrogenation of the dehydrogenated residue under  $H_2$  pressure is expected.<sup>55–85</sup> Thus, recycling and regeneration are meaningless.



**Figure 12.** Cycle of  $\text{NaBH}_4$ : ① synthesis of “new” or regenerated batches of  $\text{NaBH}_4$  by the Brown–Schlesinger process<sup>10,176</sup> using renewable energies; ②  $\text{H}_2$  generation by hydrolysis of  $\text{NaBH}_4$ ; ③ methoxylation of the borate by-products; ④ regeneration of  $\text{NaBH}_4$  following the process developed by Kemmitt and Gainsford,<sup>186</sup> but modified to use renewable energies.

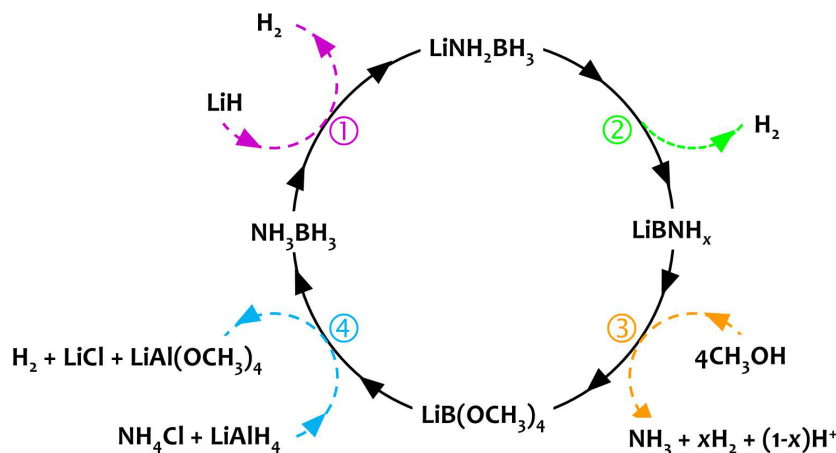
With  $\text{NH}_3\text{BH}_3$  and derivatives, storage of  $\text{H}_2$  is thermodynamically irreversible, making the recycling of the dehydrogenated residue indispensable. Two types of protocols were developed. The first ones were based on a multistep regeneration and the second ones use a single-step process.<sup>91</sup> For example, Davis et al. worked on polyborazylene as a model residue; it was first digested with benzenedithiol and the as-obtained intermediate was reduced with  $\text{Bu}_3\text{SnH}$  or  $\text{Bu}_2\text{SnH}_2$ .<sup>193</sup> In doing so,  $\text{NH}_3\text{BH}_3$  was successfully regenerated, but the process involves many chemicals and their by-products. Sutton et al. proposed a simpler approach.<sup>194</sup> Polyborazylene was rehydrogenated by  $\text{N}_2\text{H}_4$  in  $\text{NH}_3$ . Depending on the conditions, either  $\text{NH}_3\text{BH}_3$  or  $\text{N}_2\text{H}_4\text{BH}_3$  formed (Figure 13). This is one of the best achievements, but it can be applied to polyborazylene only, whereas the polymeric residue forming upon the dehydrocoupling of  $\text{NH}_3\text{BH}_3$  and derivatives is of more complex composition (mixture of polyaminoborane, polyiminoborane, *o*-polyborazylene, graphitic cross-linked polyborazylene, etc.).<sup>91,195</sup> For example, Tang et al. used the  $\text{N}_2\text{H}_4$ -based process to rehydrogenate the solid residue recovered upon the thermolytic dehydrocoupling of  $\text{LiNH}_2\text{BH}_3$  but the conversion back to  $\text{LiNH}_2\text{BH}_3$  was partial (63%),<sup>196</sup> which might be due to the presence of a fraction of polymers different from polyborazylene (Figure 13).



**Figure 13.** Regenerability of  $\text{NH}_3\text{BH}_3$  and  $\text{N}_2\text{H}_4\text{BH}_3$ : ① synthesis by salt metathesis followed by  $\text{H}_2$  evolution from  $\text{NaBH}_4$ ; ② thermolytic dehydrogenation of  $\text{N}_2\text{H}_4\text{BH}_3$ ; ③ thermolytic dehydrogenation of  $\text{NH}_3\text{BH}_3$ ; ④ hydrogenation of polyborazylene by  $\text{N}_2\text{H}_4$  in  $\text{NH}_3$  according to the process developed by Sutton et al.;<sup>194</sup> ⑤ no existing and viable hydrogenation path for the other polymeric residues.

The polymers forming upon the thermolytic dehydrocoupling of  $\text{NH}_3\text{BH}_3$  (polyaminoborane, polyiminoborane, polyborazylene) are water-sensitive. They hydrolyze, resulting in the evolution of  $\text{H}_2$  and the for-

mation of borate by-products.<sup>197</sup> The borates could be recycled according to the processes discussed above (Figure 12). A more sophisticated process, inspired by the Kemmitt and Gainsford's strategy (Eq. (28)),<sup>187</sup> was developed by Tang et al. to regenerate  $\text{LiNH}_2\text{BH}_3$  or  $\text{KNH}_2\text{BH}_3$ .<sup>198</sup> The dehydrogenated residues were digested with  $\text{CH}_3\text{OH}$ , and the alkoxyated intermediate was reduced with  $\text{LiAlH}_4$  in the presence of  $\text{NH}_4\text{Cl}$  (Figure 14). In doing so,  $\text{NH}_3\text{BH}_3$  formed. It was finally reacted with  $\text{LiH}$  or  $\text{KH}$  to complete the whole self-contained cycle.



**Figure 14.**  $\text{H}_2$  cycle with  $\text{LiNH}_2\text{BH}_3$  according to Tang et al.:<sup>198</sup> ① synthesis of  $\text{LiNH}_2\text{BH}_3$ ; ② thermolytic dehydrogenation of  $\text{LiNH}_2\text{BH}_3$ ; ③ methoxylation of the thermolytic residue  $\text{LiBNH}_x$ ; ④ formation/regeneration of  $\text{NH}_3\text{BH}_3$ .

With respect to the polyboranes used for hydrolysis or oxidation,  $\text{B}(\text{OH})_4^-$  generally forms as a by-product. The polyboranes considered as solid-state electrolytes are expected to be stable over the lifetime of the batteries. For used batteries, the polyboranes could be transformed by acidic digestion to  $\text{B}(\text{OH})_3$  or  $\text{B}(\text{OH})_4^-$ . In any case, the recycling approach summarized in Figure 12 can be applied for generating  $\text{NaBH}_4$ , which can in turn be used to regenerate the polyboranes.

### 3.4. Sodium borohydride, a “rough diamond” for Turkey

One of the riches of Turkey is boron. The reserves the country has are higher than 70% of the world's total estimated boron reserves.<sup>199</sup> A report published in 2006 gives an amount of 803 million tons.<sup>200</sup> The boron minerals that are commonly found are tincal (also called borax;  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ), and ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ). There are a number of boron products (colemanite, borax, sodium perborate, boric acid, boron element, boron nitride, boron carbide, boron halides, borates, etc.) and they are used in different areas (textile and isolation fiberglass, metallurgical agents, fertilizers, antiseptics, detergent and whiteness, glass, ceramics, military purposes, nuclear weapons, cutting tools, abrasive materials, fire retardants, medicine industry, etc.).<sup>201</sup> According to the Ministry of Energy and Natural Resources of the Republic of Turkey, the sales amount of boron products amounted to 711 million US dollars in 2016.<sup>202</sup>

The application of boron in the energy field is, however, limited to even nonexistent, whereas it has real prospects as mentioned, for example, by Balat in 2007.<sup>203</sup> Boron is a “rough diamond” for Turkey,<sup>199–203</sup> and sodium borohydride  $\text{NaBH}_4$  could be a highly important material for energy. Let us illustrate this. Assume that 100 million tons (especially borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) of the more than 800 million tons of boron minerals

are specifically dedicated to the synthesis of  $\text{NaBH}_4$ . This could be done via the so-called Brown–Schlesinger industrial process (Figure 11).<sup>10,176</sup> With a yield of 100%, 39.7 million tons of  $\text{NaBH}_4$  would be put on the market. There then would be two different uses for these 39.7 million tons. First,  $\text{NaBH}_4$  is a liquid-state hydrogen storage material. With the amount calculated above,  $\text{NaBH}_4$  and  $\text{H}_2\text{O}$  would be able to release 4.3 million tons of  $\text{H}_2$  each (Eq. (1)), which means a total of 8.6 million tons. The theoretical specific energy of  $\text{H}_2$  at ambient pressure is  $8890 \text{ Wh kg}^{-1}$  (for an  $\text{H}_2/\text{O}_2$  fuel cell).<sup>3</sup> Hence, with 8.6 million tons of  $\text{H}_2$ , the theoretical specific energy would amount to 77 TWh. Second, the aqueous alkaline solution of  $\text{NaBH}_4$  is a potential fuel of direct liquid-fed fuel cells. The theoretical specific energy of the direct borohydride fuel cell is  $9295 \text{ Wh kg}^{-1}$ .<sup>114</sup> Hence, with 39.7 million tons of  $\text{NaBH}_4$ , a theoretical specific energy of 369 TWh would be expected. The specific energies of 77 and 369 TWh are theoretical. To be more realistic, they may be revised downwards. To the knowledge of the author, there are no data to be exploited to make more realistic calculations. Therefore, for the present discussion, the theoretical specific energies will just be divided by 2 (50% of efficiency, which is a bit higher than the best values of diesel engines<sup>204</sup>). Accordingly, with 100 million tons of borax, specific energies of 38.5 and 184.5 TWh could be achieved, respectively. For comparison, one may cite the electricity production potential of the R.E. Ginna nuclear power plant in New York (the smallest plant in the United States); it operates at 508 MW.<sup>205</sup> With the 39.7 million tons of  $\text{NaBH}_4$ , one may have, respectively, a capacity of about 8.6 and 41.5 power plants delivering electricity 24 h a day for 1 year (without any stop).

The implementation of  $\text{NaBH}_4$  and related boron-based materials only makes sense if these materials, especially  $\text{NaBH}_4$ , are regenerated (Figures 12 and 13). As mentioned by Liu and Chen<sup>176</sup> and Monteverde and Magistri,<sup>192</sup>  $\text{NaBH}_4$  could be competitive provided the production and regeneration processes use renewable sources like wind power and solar power. The high potential of renewable energies (the other riches of the country) for the Turkish economy and energy independence have been discussed in a number of articles within the past two decades.<sup>206–220</sup> For example, solar energy (either photovoltaic or concentrating solar power) could be a very relevant way to regenerate  $\text{NaBH}_4$  with the objective of lowering the costs.

The energy cycle with  $\text{NaBH}_4$  or any other boron-based materials is crucial for two reasons. The first one is obviously sustainability. It is important not to generate unrecyclable wastes. A waste (i.e. a by-product) must be seen as a “raw” material for regenerating the starting material. The second reason is to have an inexhaustible energy carrier. The amounts are clearly limited to the boron reserves but part of them (e.g., 100 million tons) may be “indefinitely” used. For  $\text{NaBH}_4$  as a liquid-state hydrogen storage material, this would be comparable to 8.6 power plants in continuous activity. This would be one of the solutions for the energy independence of Turkey.

Sodium borohydride is a “rough diamond”. It still needs to be “cut” in order to be viable, implementable, and competitive. The other boron-based materials are “rougher”, except ammonia borane as a solid-state hydrogen storage material. In any case, they all have to be further investigated and developed in order to overcome the technical and scientific challenges, reduce the overall cost of the final technology, and define the final applications. In such a context, Turkey has everything to gain by making sodium borohydride and any other boron-based material common energy carriers/materials.

#### 4. Conclusion

Within the past two decades, boron-based materials have been considered as having a potential in the field of energy. Most of them have been reported in the present review and their respective potentials in four different applications have been discussed. It stands out that there are selected materials for liquid-state and/or solid-state hydrogen storage; others are more suitable as liquid fuels of direct liquid fed-fuel cells, and a few have prospects as solid electrolytes of Li-/Na-ion batteries and/or hypergolic fuels. Of all of them, one clearly emerges: sodium borohydride. It has been much investigated for hydrogen storage and as a liquid fuel, and today prototypes exist for both applications. Furthermore, it is or it may be the precursor of all of the other boron-based materials. With such features, sodium borohydride  $\text{NaBH}_4$  stands as the leading boron-based material for energy. With more efforts at both laboratory and industrial scales, it could be one of the leading energy technologies. This would be especially of benefit for Turkey, a country that has more than 70% of the world's total estimated boron reserves, with more than 803 million tons. A simple analysis shows that sodium borohydride could represent the capacity of dozens of plants of small scale. However, the viability and implementation of sodium borohydride are strongly dependent on the possibility to regenerate it from the spent fuels at low cost thanks to the use of renewable energies like the sun. In conclusion, sodium borohydride and more widely boron-based materials are “rough diamonds” for Turkey.

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