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Account / Revue

Sodium tetrahydroborate as energy/hydrogen carrier, its history

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Abstract

Sodium tetrahydroborate $NaBH_4$ is considered as being a promising energy/hydrogen carrier. $NaBH_4$ is not a new compound. It has been discovered in 1940s by Prof. H.C. Brown, Nobel Laureate in Chemistry in 1979. $NaBH_4$ has thus a history and this history distinguishes the $NaBH_4$ utilisation as hydrogen carrier from that as energy carrier. In fact, the history of $NaBH_4$ (for both utilisations) can be divided into three periods, each period being characterised by specific societal challenges. Whereas during the first period the challenges were military and political, the challenges in the third period (i.e. at present) are energetic, environmental, civilian, social and political. The second period was rather calm for $NaBH_4$ even if it was intensively used as a reducing agent in organic chemistry. *To cite this article: Umit B. Demirci, P. Miele, C. R. Chimie 12 (2009).*
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Résumé

Dans un monde confronté à des problèmes majeurs dans les domaines énergétiques et environnementaux, le tétrahydroborate de sodium $NaBH_4$ semble être un matériau prometteur comme vecteur d'hydrogène ou comme vecteur d'énergie. $NaBH_4$ a été découvert dans les années 40 par le Prof. H.C. Brown, qui reçut le prix Nobel 1979 de Chimie. $NaBH_4$ a une double histoire: une comme vecteur d'hydrogène et une comme vecteur d'énergie. Ces histoires sont relatées par le présent article. Ces deux histoires peuvent se distinguer en trois périodes, chacune de ces périodes elles étant caractérisée par des défis sociétaux spécifiques. Alors que pendant la première période les défis étaient militaires et politiques, les défis de la troisième période sont énergétiques, environnementaux, civils, sociaux et politiques. La seconde période fut calme pour $NaBH_4$ en tant que vecteur d'hydrogène ou d'énergie, mais celui-ci fut très utilisé comme agent réducteur en chimie organique. *Pour citer cet article : Umit B. Demirci, P. Miele, C. R. Chimie 12 (2009).*
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1. Introduction

In less than ten years, a well-known chemical has become a promising compound in energy. This chemical is recognised to have a high potential as energy/hydrogen carrier. Energy is today a central concern because of resource (i.e. oil) depletion and global climate change (i.e. global warming due to greenhouse gases like e.g. carbon dioxide CO_2) and that is why sustainable energy carriers are being investigated. It is expected from the sustainable energy carriers that they are renewable and they do not emit CO_2. For some sustainable energy carriers (e.g. the chemical introduced above, hydrogen or methanol) technologies intended to convert their chemical energy into electrical energy are being developed and in such a context the hydrogen-powered fuel cell stands out. In relation to conventional sources of energy like e.g. the heat engine, the fuel cell shows four major potential benefits [1]:

- higher overall efficiency;
- minimised pollution, the by-product being water;
- possibility of obtaining the fuel from renewable resources;
- better reliability.

The fuel cell is even considered as being a green technology [2]. Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) can be powered, directly or indirectly, by the chemical introduced above.

What is this chemical? It is sodium tetrahydroborate $NaBH_4$. It is especially known as a reducing agent and it is much used in organic chemistry. In industry, it is a specialty reducing agent in the manufacture of pharmaceuticals and a bleaching agent in the manufacture of paper. Now it is also known as an energy/hydrogen carrier. It is an energy carrier when it directly powers a PEMFC-type fuel cell, which is called direct borohydride fuel cell (DBFC) [3]. It is a hydrogen carrier when it stores and releases hydrogen that is intended to power a PEMFC [4]. In other words $NaBH_4$ can directly or indirectly power a PEMFC.

$NaBH_4$ is not a new compound since it was discovered in 1940s.[1] $NaBH_4$ as energy carrier and $NaBH_4$ as hydrogen carrier have a history. This history can be divided into three periods of about 20−30 years each:

- a first splendour period, the 20 years that follows its discovery;
- a second period, a much quieter period of about 30 years;
- a third period, the present period that is characterised by an intense research activity and by the development of prototypes.

The history of a chemical can be interesting and its knowledge may be important for the present investigations. Hence the present paper relates the history of $NaBH_4$ as energy/hydrogen carrier.

2. Preliminaries

2.1. Prof. H.C. Brown, Nobel Laureate in Chemistry 1979

Prof. H.C. Brown (1912−2004) and Prof. H.I. Schlesinger were the inventors of $NaBH_4$. Prof. H.C. Brown has been awarded the Nobel Prize in Chemistry in 1979 "for the development of use of boron-containing compounds into important reagents in organic synthesis."[2] In 1979 the Nobel Lecture provided Prof. H.C. Brown the opportunity to trace his research program in boron-containing compounds from its inception in 1936.[1] It is worth reporting below several passages[1] because they are relevant for drawing the context in which $NaBH_4$ was discovered.

In 1940, Schlesinger and Brown, who were chemists at the University of Chicago, were "requested to undertake for the National Defence Research Committee [of the United States] a search for new volatile compounds of uranium of low molecular weight." Their laboratory had at that time a significant experience in the synthesis of volatile compounds such as aluminium tetrahydroborate $Al(BH_4)_3$ [5] and beryllium tetrahydroborate $Be(BH_4)_2$ [6], which were the most volatile compounds known for these elements. At the same time, lithium tetrahydroborate $LiBH_4$ [7] was synthesised but it was a typical non-volatile salt-like compound. Gallium tetrahydroborate $Ga(BH_4)_3$ was also envisaged but with much less success [8]. Then Schlesinger and Brown undertook to synthesise uranium(IV) tetrahydroborate and the attempt was successful [9]. Unfortunately they "were informed that the problems of handling uranium hexafluoride had been overcome and there was no longer any need for uranium tetrahydroborate." They decided then to disband their group "when the Army Signal Corps informed [them] that the

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new chemical sodium tetrahydroborate appeared promising for the field generation of hydrogen. However a more economical mean of manufacturing the chemical was required.''

The potential of $NaBH_4$ as hydrogen generator was thus remarked in a military context. A former initiative of the military research is at the origin of the present emergence of a technology that is intended for civilian applications.

2.2. Periods of the history of NaBH₄

Further to the first Schlesinger and Brown's work,[1] many experimental articles about $NaBH_4$ were published. The twenty years that followed the invention of $NaBH_4$ were characterised by intense investigations. Then the research about $NaBH_4$ as energy/hydrogen carrier stopped. Very few papers were published. At that time, $NaBH_4$ was much more interesting as a reducing agent. During the second period, the oil crisis that arose was in a way the beginning of the energy crisis that we are living at present. Today scientists have accepted a challenge that is to find alternate energies to the fossil fuels. Hence, in the late 1990s $NaBH_4$ has drawn scientists' attention to itself again. It has been the beginning of the third (present) period.

2.3. NaBH₄ as energy/hydrogen carrier

$NaBH_4$ has first been viewed as a hydrogen generator since it can generate molecular hydrogen from its hydrogen atoms.[1] On the other hand it is also an energy carrier since it can generate electrons (i.e. electricity). In other words $NaBH_4$ carries energy in two ways, i.e. indirectly and directly. Accordingly, it is essential to distinguish these ways.

$NaBH_4$ stores atomic hydrogen (10.7 wt%) and can generate molecular hydrogen by hydrolysis [4]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2.$$
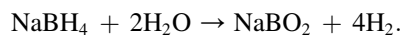
Molecular hydrogen can also be generated by thermolysis at high temperatures [10]. In consequence $NaBH_4$ is a hydrogen carrier. Generated hydrogen can be used to power a PEMFC [4]. In that case, $NaBH_4$ is an indirect fuel.

$NaBH_4$ can have an anodic behaviour. In an alkaline medium and in the presence of a catalyst, it can be oxidised as follows:

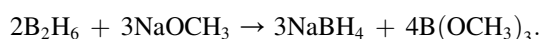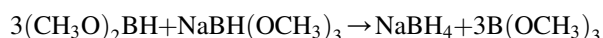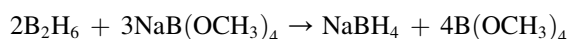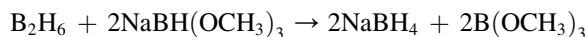$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-.$$

This oxidation reaction is the fundamental of the DBFC [3]. In that case, $NaBH_4$ is a direct fuel and thus an energy carrier (or also an electron carrier).

3. History of NaBH₄

3.1. First period 1942–1965

3.1.1. Discovery of NaBH₄

According to Brown, $NaBH_4$ was discovered in 1942.[1] The paper dealing with the discovery was published in 1953 [11]. Schlesinger et al. [11] explored four $NaBH_4$ synthesis routes whose chemical equations are as follows:

$$B_2H_6 + 2NaBH(OCH_3)_3 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$$

$$2B_2H_6 + 3NaB(OCH_3)_4 \rightarrow NaBH_4 + 4B(OCH_3)_4$$

$$3(CH_3O)_2BH + NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3B(OCH_3)_3$$

$$2B_2H_6 + 3NaOCH_3 \rightarrow 3NaBH_4 + 4B(OCH_3)_3.$$

In a further paper, a simpler method of $NaBH_4$ preparation consisting of the rapid reaction at 225–275 °C of sodium hydride with methyl borate was reported [12]:

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3.$$
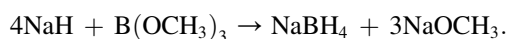
In 1979, Brown commented that this reaction provided ''the basis for the present industrial process for the manufacture of sodium tetrahydroborate.''[1]

$NaBH_4$ is a white crystalline solid of remarkable stability, not showing apparent change when heated in air to 300 °C and in vacuum to 400 °C [11]. $NaBH_4$ dissolves in cold water without extensive reaction [11].

3.1.2. NaBH₄, a hydrogen generator

According to Schlesinger et al. [11], $NaBH_4$ reacted slowly with water to liberate 4 mol of hydrogen per mole of $NaBH_4$ or 2.4 l/g at room temperature. The reaction could be greatly accelerated by temperature rise or by addition of acids/catalysts. These observations are historically crucial because they introduce two features that are important today:

- $NaBH_4$ generates hydrogen,
- the generation of hydrogen can catalytically be accelerated.

The catalytic effects of more than 20 acids and of certain metal salts (manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) chlorides) were tested [13]. Papers entirely devoted to the $NaBH_4$ hydrolysis were published. Levy et al. [14] reported that the $CoCl_2$-catalysed hydrolysis was a first-order reaction with

respect to the $NaBH_4$ concentration and that an application of kinetic data should permit a selection of the catalyst concentration to give the desired hydrogen generation rates. Brown and Brown [15] showed that many of the heavy metals exerted a powerful catalytic effect on the hydrolysis of $NaBH_4$. The platinum family metals were unusually effective with Ru, $Rh > Pt > Co > Ni > Os > Ir > Fe \gg Pd$, at 25 °C. $NaBH_4$ reduced the platinum metals to the elementary state, in a form which exhibited high catalytic activity for the hydrolysis reaction. Davis et al. [16] focused on the hydrolysis catalysed by general acids:

$$BH_4^- + H_3O^+ + 2H_2O \rightarrow H_3BO_3 + 4H_2.$$
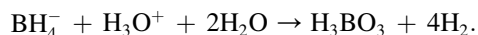
The reaction order was unity in the $NaBH_4$ concentration and unity in the concentration of the acid.

Studies attempting to understand the reaction kinetics and mechanisms were published [16–19]. The reaction mechanisms that were proposed are not reported here.

The generation of hydrogen in other solvents like e.g. alcohols [20] was also assessed. Davis [21] investigated the reaction of $NaBH_4$ with methanol (methanolysis). Hydrogen gas was produced in accordance with the following reaction:

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2.$$
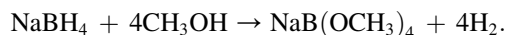
The reaction order versus the $NaBH_4$ concentration was of one. It was besides reported that the addition of an acid increased the rate of methanolysis while basic materials decreased it.

3.1.3. NaBH₄, a reducing agent

$NaBH_4$ is able to rapidly reduce acetone and so it is a reducing agent for organic and inorganic compounds [11]. Brown[1] focused on the "means of increasing the reducing properties of sodium tetrahydroborate." A problem with $NaBH_4$ in its utilisation in organic chemistry was the lack of suitable solvents. Brown and co-workers [20,22] studied some solvents to favour the reactivity of acetone with $NaBH_4$. It was found that 2-propanol was a convenient solvent with a $NaBH_4$ solubility of $3.7 \, g \, l^{-1}$ at 25 °C while the $NaBH_4$ solubility in 2-methyl-2-propanol was $1.1 \, g \, l^{-1}$ at 25 °C. Moreover $NaBH_4$ was slightly soluble in monoglyme but highly soluble in both diglyme and triglyme.

3.1.4. NaBH₄ properties

Researchers were otherwise interested in the properties of $NaBH_4$. In 1949, whereas Schlesinger et al. [11] had yet not published their invention, Davis et al.

[23] determined the value for the standard heat of $NaBH_4$ formation ($-183.51 \, kJ \, mol^{-1}$). Few years later, Johnston and Hallett [24] measured its heat capacity from -258 to 27 °C. Stockmayer et al. [25] determined the standard free energy change of the reaction

$$NaBH_4(s) \rightarrow Na^+ + BH_4^-$$
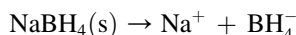
at 25 °C ($-23.7 \, kJ \, mol^{-1}$), the standard free energy of formation of aqueous BH_4^- ($119.7 \, kJ \, mol^{-1}$), the standard entropy of the ion (estimated to $25.5 \pm 1.0 \, J \, K^{-1}$) and the polarizability of tetrahydroborate in its alkali salt ($3.94 \, Å^{-3}$). From a theoretical calculation, Altschuller [26] determined a polarizability of $3.90 \, Å^{-3}$. Moreover a heat of formation of gaseous BH_4^- (g) was calculated as being $-403.2 \, kJ \, mol^{-1}$. Gunn and Green [27] measured the heat of solution of $NaBH_4$ ($-3.3 \, kJ$ at 25 °C) and then derived both the formation heat and the entropy of the ion ($43.5 \, kJ$ and $26.3 \, J \, K^{-1}$, respectively).

3.1.5. NaBH₄, an energy carrier

The oxidation of tetrahydroborate was another way of valorising the energy potential of $NaBH_4$. It is often noticed that the DBFC was first proposed in the early 1960s (see e.g. Ref. [28]), and especially by Indig and Snider [29]. However, it is important to note here that in 1953 Pecsok [30] proposed for the polarographic oxidation of $NaBH_4$ the net reaction:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-.$$

The standard electromotive force of this half reaction was calculated as being 1.23 V versus the standard hydrogen electrode and it was observed that the $NaBH_4$ oxidation was irreversible. Two years later, Stockmayer et al. [25] calculated a value of 1.24 V.

Indig and Snider [29] are considered as being the first researchers having proposed the DBFC concept because they suggested that "the possibility of using sodium tetrahydroborate as an anodic fuel appeared attractive due to its extremely low equivalent weight of 4.73 g." A practical demonstration of direct electricity generation from tetrahydroborate ions had been reported. However, according to Indig and Snider the possibility of achieving a reversible sodium tetrahydroborate electrode with an 8-electron oxidation appeared unlikely and that one might have to settle for a reaction involving 4-electron change

$$BH_4^- + 4OH^- \rightarrow BO_2^- + 2H_2 + 2H_2O + 4e^-$$
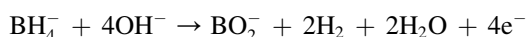
and a lower potential. The competition between the electrochemical oxidation of BH_4^- and the hydrolysis of

BH_4^- was also reported by Elder and Hickling [31]. Elder [32] showed that the condition that decides which of the two processes occurs is not the pH but the relative proportion $[BH_4^-]/[OH^-]$.

3.1.6. End of the first period

Gardiner and Collat's article about the $NaBH_4$ hydrolysis [19] and Indig and Snider's paper about the $NaBH_4$ electrooxidation [29] can be considered as the publications that ended the first period 1942–1965. An intense activity in exploratory/fundamental research characterised this period. Because $NaBH_4$ drew the U.S. Army's attention, the applied research has remained secret.

During this period, $NaBH_4$ showed that it was a potential hydrogen carrier as well as a potential energy carrier. Because $NaBH_4$ had first drawn attention for its ability to store/generate hydrogen, the efforts devoted to the $NaBH_4$ hydrolysis were more important than those devoted to the $NaBH_4$ electrooxidation. However $NaBH_4$ as energy/hydrogen carrier was not beyond a period that forgot it.

3.2. Second period 1966–1998

The second period 1966–1998 was quite calm for $NaBH_4$ as energy/hydrogen carrier. Nevertheless $NaBH_4$ was much used as reducing agent in the synthesis of organic chemical compounds [33].[1]

In this calmer period, the investigations did not completely stop. Holbrook and Twist [34] investigated the hydrolysis of $NaBH_4$ catalysed by nickel–boron and cobalt–boron alloys. By using deuterium oxides D_2O and analysing the gas evolved, it was confirmed that approximately half the hydrogen evolved originates from $NaBH_4$ and half from H_2O. However, unlike the studies reported in the previous sections it was observed that the reaction order versus the $NaBH_4$ concentration was zero. In 1980s, Kaufman and Sen [35] undertook a new study in order to investigate the potential of $NaBH_4$ as a precursor fuel source for a hydrogen–oxygen (air) fuel cell. Acids (like perchloric acid, oxalic acid, etc.), transition metals (like Co, Ni, Mn, etc.) and salts of these metals were studied. As that was expectable these materials markedly activated the $NaBH_4$ hydrolysis and so the hydrogen generation.

Walker [33] studied the $NaBH_4$ solubility. It was reported a high solubility in water, methanol, ethanol and 2-methoxyethyl ether. $NaBH_4$ was lowly soluble in both diethyl ether and tetrahydrofuran. It was observed that $NaBH_4$ reacted rapidly with methanol but slowly with ethanol. According to Walker, for most purposes ethanol is the preferred solvent because an ethanolic solution of $NaBH_4$ possesses the advantages of a homogeneous solution together with little loss of the reducing agent through side reaction with the solvent; on the other hand, in 2-methoxyethyl ether, $NaBH_4$ is an exceptionally mild reducing agent, which reduces aldehydes but not ketones.

The 1960s was an eventful decade. Numerous events have sharply affected society in all of its aspects: from social and politics to culture, via science and technologies. At that time, energy was not a concern and that lasted until 1973, that is, the beginning of the oil crisis. The industrialised countries realised they were completely dependent on crude oil, a depleting resource. Furthermore fossil fuels were at the origin of significant environmental issues such as the ozone depletion and the global warming. In 1997, the Kyoto protocol that aims at reducing emissions of greenhouse gases was agreed. In 1998, the twelve principles of green chemistry were postulated [36]. It is in this context that scientists have to find energy sources as alternatives to fossil fuels. These energies have to be renewable (and/or green). Hydrogen and fuel cells are potential candidates. With respect to $NaBH_4$, the late 1990s are clearly the beginning point of the third period, which is characterised by the revival of the scientific/technological interest towards $NaBH_4$ as energy/hydrogen carrier.

3.3. Third period 1999–…

3.3.1. Context

The context in which the investigations about $NaBH_4$ as energy/hydrogen carrier started again was critical from both energy and environment points of view. Nevertheless, this context was much favourable to the emergence of new energy sources.

In 1999, Amendola et al. [37] opened the third period of $NaBH_4$. This new period is completely different from the first one. Indeed Amendola et al. are civilian researchers working for Millennium Cell,[3] a U.S.-based public company "that develops hydrogen battery technology through a patented chemical process that safely stores and delivers hydrogen energy to power portable devices." The patented chemical process is none other than the $NaBH_4$ hydrolysis. In 2000, Amendola et al. [38]

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[3] All information related to the Hydrogen on Demand® technology patented and produced by the society Millennium Cell are available on the website http://www.millenniumcell.com.
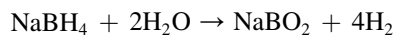
published a work dealing with the production of hydrogen from stabilised $NaBH_4$ solution. High hydrogen generation rates can be achieved from $NaBH_4$ solutions with tiny amounts of Ru supported on anion exchange resins. The first patent issued on boron based technology Hydrogen on Demand® Power PEM Fuel Cell dates from 1998. From that moment, Millennium Cell has developed collaborations with several societies. For example, in 2000, the society announced relationship with Daimler Chrysler that was followed by the construction of a prototype vehicle equipped with their technology. Millennium Cell is working on the $NaBH_4$ hydrolysis [38] as well as on the $NaBH_4$ electrooxidation [37].

Nowadays, $NaBH_4$ as hydrogen carrier must take up an economic challenge, in addition to the energetic, environmental challenges. Unlike the first period 1942–1965, the third period faces energetic, environmental emergencies as well as social, political challenges. Hydrogen from $NaBH_4$ is mainly intended to civilian applications and research is much more applied than that of the 1940–1950s. Accordingly much more effort is today devoted to $NaBH_4$ as hydrogen carrier but also to $NaBH_4$ as energy carrier.

3.3.2. NaBH₄ as hydrogen carrier

$NaBH_4$ is regarded as a promising hydrogen storage material [10,39] but $NaBH_4$ as hydrogen carrier faces some significant issues. In a review dealing with the state of the art of the NaBH4 hydrolysis, Wee et al. [4] reported that in order that the $NaBH_4$–PEMFC system becomes an alternative system of supplying hydrogen in fuel cells some issues should be solved. These issues are the deactivation of the catalyst, the treatment of the by-products, the proper control of the reaction rate and the price of $NaBH_4$. In fact, besides the price issue (discussed below because it is also the issue of $NaBH_4$ as energy carrier) there are three main issues that really hinder the development of $NaBH_4$ as hydrogen carrier.

The first issue [40], which is likely to be the main issue, is that the hydrolysis reaction does not follow the ideal route given by the reaction

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

but it is rather as

$$NaBH_4 + (2 + x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2.$$
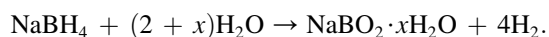
The reaction by-product is hydrated with x molecules of water what decreases the gravimetric

hydrogen storage capacity from about 11 wt% to 4–7 wt%. Investigations are in progress to improve and optimise these low values.

The second issue is the catalyst efficiency (reactivity and resistance to deactivation). The performance of the catalysts have already been reviewed [4,41]. In short, their resistance does not seem specifically investigated, what is regrettable, while their reactivity has largely been studied.

The third issue is the post-treatment of the hydrolysis by-products (anhydrous and hydrated $NaBO_2$). $NaBH_4$ is a non-reversible chemical hydride. Hence a way for recycling $NaBO_2$ into $NaBH_4$ is being investigated. This is very important. If $NaBO_2$ cannot be recycled, $NaBH_4$ cannot be regarded as a sustainable or renewable (or rather recyclable) material what will then imply an inevitable issue of boron resources depletion. Furthermore, recycling $NaBO_2$ might contribute to the decrease of the $NaBH_4$ price. Investigations are in progress. For example, Kojima and Haga [42] investigated various routes for synthesising $NaBH_4$ from the by-product $NaBO_2$:

- annealing of a mixture of $NaBO_2$ with magnesium hydride under high hydrogen pressure, i.e. $NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO$,
- annealing of a mixture of $NaBO_2$ with magnesium silicide under high hydrogen pressure, i.e. $NaBO_2 + 2Mg + Si + 2H_2 \rightarrow$ $NaBO_2 + Mg_2Si + 2H_2 \rightarrow NaBH_4 + 2MgO + Si$,
- reaction of $NaBO_2$ with coke, i.e. $NaBO_2 + 2C + 2H_2O \rightarrow NaBH_4 + 2CO_2$,
- reaction of $NaBO_2$ with methane, i.e. $NaBO_2 + 2CH_4 + 2H_2O \rightarrow$ $NaBH_4 + 2CO_2 + 4H_2$.

Note that the reaction of sodium hydride with boric oxide has been used for commercial production of $NaBH_4$ [43]:

$$4NaH + 2B_2O_3 \rightarrow NaBH_4 + 3NaBO_2.$$
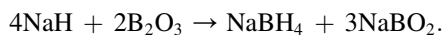
Researchers are working to solve these issues. Interestingly Zanchetta et al. [44] even proposed an article in which an integrated apparatus for the production and measurement of hydrogen from $NaBH_4$ is completely described. This article is a good example of the significance of the researchers' implication. Some studies have a significance that is more fundamental than applied while others are about much more applied work. However, that may be, the objective of all of the published papers is similar, that is, to propose

a technological solution for being commercialised. The fundamental studies especially focus on the reaction kinetics (for details and references, see e.g. [45]) and the reaction mechanisms (e.g. [46]). Globally the kinetic data recently proposed have confirmed those found during the first period. For instance, a first-order reaction with respect to $NaBH_4$ concentration was suggested in 1960s [14,16] and is today often confirmed [45]. On the other hand the reaction mechanisms that are being suggested are rather new [46].

3.3.3. NaBH₄ as energy carrier

Amendola et al. [37] reported the performance of a DBFC using an Au−Pt-based anode electrocatalyst and showed that DBFC is an extremely attractive power source. Since that work, many papers about $NaBH_4$ as energy carrier have been published but the DBFC (in other words $NaBH_4$ as energy carrier) is facing issues. Ponce de Leon et al. [47] reviewed the recent and rapid progress in the development of the DBFC and according to these authors the results are encouraging although more research is necessary. Wee [28] also reviewed the DBFC and compared it to the direct methanol fuel cell (DMFC). The relative competitiveness of both fuel cells given the current status of the technologies and assuming some generally accepted conditions were analysed. According to Wee, the DBFC is superior to the DMFC in terms of cell size and fuel consumption but the total operating costs of the former are higher. Recently Demirci [3] listed the main issues facing the DBFC and stressed three of them:

- the occurrence of the tetrahydroborate hydrolysis,
- the occurrence of the tetrahydroborate crossover,
- the high cost of $NaBH_4$.

These issues had also been suggested by Ponce de Leon et al. [47] and Wee [28] but Demirci [3] especially focused on the membrane-electrode assembly for discussing about them and attempted to propose potential solutions. The solutions are e.g. Au-based catalysts, more selective membranes and cheaper materials, respectively.

The studies devoted to $NaBH_4$ as energy carrier focus more on applied aspects than on fundamental ones. There are however some fundamental studies (for details and references, see e.g. Ref. [3]). To illustrate this purpose, a typical example may be cited. It was showed that the $NaBH_4$ electrooxidation does in fact not involve 8 electrons, the number of electrons being rather 4 because of the occurrence of the $NaBH_4$ hydrolysis, which is a side reaction in that case [3].

The occurrence of a competition between the $NaBH_4$ electrooxidation and the $NaBH_4$ hydrolysis had been reported in 1960s [29,32].

Nowadays prototypes have been constructed or are being produced. The first demonstration of a DBFC for laptop computers was presented in 2005 by MERIT (Materials and Energy Research Institute) [48]. At that time the production of a prototype was a significant progress.

3.3.4. NaBH₄ cost

Interestingly Wee [49] compared $NaBH_4$ as hydrogen carrier intended to the PEMFC to $NaBH_4$ as energy carrier powering the DBFC. This comparative analysis considered the current technologies and the high price of $NaBH_4$, and evaluated the factors influencing the relative favourability of each type of fuel cells. It is reported that the competitiveness is strongly dependent on the extent of the $NaBH_4$ crossover. When the crossover is taken into account, the PEMFC is the most competitive. If the problem of crossover is to be completely overcome, the total cost of the DBFC generating 6 electrons is very similar to that of the PEMFC. Above all the DBFC generating 8 electrons is the most competitive.

Wee largely tackled the cost issue in his three papers [4,28,49]. According to Wee [49], "the current high price of $NaBH_4$ (U.S. \$55 kg^{-1}) presents a serious restriction to the development of borohydride as an economically viable method of H_2 storage and/or generation […]. The pure price of H_2 generated from $NaBH_4$ […] is about 130 times higher than that of H_2 generating via the reforming of natural gas […]. The required cost reduction may be achievable via the new processes of $NaBH_4$ synthesis, mass production and the recycling of the reaction product $NaBO_2$."

3.3.5. Perspectives

The research devoted to $NaBH_4$ is active and vivid. It is catalysed by the societal challenges that are very different from those in the first period. Today the challenges are energetic, environmental, civilian, social and political. Yesterday they were mainly military. For many researchers, $NaBH_4$ has a great potential either as a hydrogen carrier or as an energy carrier. Prototypes already exist. Marketing is even announced… but that is not yet history.

4. Conclusion

Today $NaBH_4$ is recognised to have a great potential in the energy field. It has even a double potential. First,

$NaBH_4$ is considered as a hydrogen carrier since it stores 10.7 wt% of atomic hydrogen and can hydrolyse generating molecular hydrogen (half of hydrogen being provided by water). Second, $NaBH_4$ is considered as an energy carrier as its electrooxidation generates 8 electrons that can be used in a fuel cell. Hence $NaBH_4$ is a fuel that can indirectly power a PEMFC (hydrogen is the fuel) while it is a fuel that can directly power a DBFC.

$NaBH_4$ is known to be an energy/hydrogen carrier since 1940s. $NaBH_4$ has thus a history. It has a history as energy carrier and it has a history as hydrogen carrier. Note that it has also a history as reducing agent in organic chemistry. The histories as energy/hydrogen carrier can be divided into three distinct periods. Each period is characterised by specific societal challenges. Whereas the challenges in the first period were military and political, the challenges in the third (present) period are energetic, environmental, civilian, social and political. The second period was calm for $NaBH_4$ as energy/hydrogen carrier but it was largely used as reducing agent in organic chemistry. Today the research is much more applied than that in the 1950–1960s but the basic issues are still the same. With respect to the fundamental studies, the third period generally confirms the fundamental findings reported in the first period. In fact with the passing decades only the global context has changed.

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