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Sodium Borohydride Hydrolysis as Hydrogen Generator: Issues, State of the Art and Applicability Upstream from a Fuel Cell — Source link

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RESPONSE TO THE COMMENTS MADE BY THE REFEREES

Review Editor: Wagner, Frederick

Many apologies for the delays in handling this paper. We received one thoughtful review but were not able to get reviews from others working in this area. Much too much time has gone by, so we must proceed on the basis of the one review we have. Please carefully consider the review, noting the required revisions and the reviewer's list of topics that are probably more important than the ones concentrated upon in your manuscript. If you can at least mention these topics in a revised manuscript, we may be able to publish this as a review paper.

Dear Editor,

First of all I would like to thank you and the reviewer for having referred our manuscript which title is given above. I carefully considered the review. With respect to it, I have actually two comments:

- **The original version of the manuscript was not clear enough in stating its objective. Indeed the objective was to review the $NaBH_4$-devoted literature while focusing on the issues. But most of the published studies deal with either the catalyst used in the hydrolysis or the storage capacity of the system $NaBH_4$-H_2O. Hence, our manuscript mainly tackled these two issues. As a result of such misunderstanding, we have added in the revised version of the manuscript few lines at page 2 for making clear the paper objective. Moreover, we have made clear the first words of the title that might also lead to such a misunderstanding.**
- **Some of the issues that have been suggested by the Reviewer are relating to the storage system. Unfortunately we have never worked on a storage system and moreover there are very few documents about such a technology. It was therefore difficult for us to tackle such issues in the original version of the paper. Nevertheless the Reviewer's comments have been helpful to find some pieces of information and accordingly the issues suggested have been briefly discussed throughout our revised manuscript.**

All of the Reviewer's comments have been considered and our comments to the comments are given in details hereafter. Our manuscript has been revised and we provide two versions of it, the first one shows the modifications in yellow and the second one is the revised manuscript in black and white (i.e. without the yellow colour).

We hope that this revised version will be accepted in your valuable journal *Fuel Cells*. We are at your disposal for any further question.

Dr. Umit B. DEMIRCI

Reviewer: 1

The paper as presented is an accurate and well presented literature search. However, no significant or new conclusions are proposed in this paper. Furthermore, some of the key issues preventing the *use of NaBH4 in automotive systems were not adequately investigated or described. In general, I agree with the authors' conclusions, however, I don't believe the full picture was provided.*

Dear Reviewer,

First of all we would like to thank you for your efforts in referring our manuscript. We have taken into consideration all of your comments and made the changes. These are listed hereafter.

Dr. Umit B. DEMIRCI

The Author concentrates on only two of several issues.

Actually we were not clear enough in stating the objective of our manuscript. Indeed the objective was to review the $NaBH_4$-devoted literature while focusing on the issues. But most of the published studies deal with either the catalyst used in the hydrolysis or the storage capacity of the system $NaBH_4$-H_2O. Hence, our manuscript mainly tackled these two issues. As a result of such misunderstanding, we have added in the revised version of the manuscript few words/lines in the abstract and at page 2 for making clear the paper objective.

o *Water balance handling (only from a gravimetric weight density perspective)*

A paragraph about the volumetric hydrogen storage capacity has been added at pages 6 and 13. It explains why this parameter is not discussed within our manuscript and also throughout the $NaBH_4$-devoted open literature.

o *Efficiency of catalyst – from experience, this was not a major issue for us. We routinely achieved 99% yield with very fast light off times <30 seconds in most cases with the Millenium Cell system. Once warmed, system kinetics or conversion yield was not a problem for us. In fact we believe our reactor chamber was grossly oversized due to the efficiency of the catalyst- for that reason, the catalyst cost in the chamber does not represent a major portion of the expense of the system. The author is correct in highlighting the durability issues of the catalyst – we experienced a high washout rate*

With respect to the catalyst reactivity and its cost, we have been more cautious in the discussion. Few lines have been added at pages 12-13 to ask a question about the catalyst cost. However, we have not been able to discuss in depth this cost 'issue' because of a lack of information throughout the open literature.

With respect of the catalyst durability, the discussion stresses on the issue (see e.g. the abstract and section 4.1).

Other issues – I believe are equally or more important

The other issues have been briefly tackled in a new section (4.2) at the end of the manuscript (page 13).

Waste NaBO2 recycling- The author briefly acknowledges the issue but decides not to concentrate on it- The issue of recyclability played a central role in the no-go decision for the DOE- The author should refer to work done by Rohm& Hass under the FreedomCar H2 Storage Program (completed in 2008) that exhaustively investigated possible regeneration routes- none of which proved feasible (i.e >60% regeneration efficiency based on LHV of H2)

It is true that this issue is significant. For example, it is one of the issues having led to the no-go for $NaBH_4$ in automotive applications. Nevertheless, in terms of publications, this issue seems not to interest as both the catalytic material and the hydrogen density do. This

issue has not been discussed more in details for the reasons given above. However that may be, few lines have been added at page 13 and few references have been given for the reader interested by this issue.

Heat rejection – As stated in the paper, the hydrolysis of NaBH4 is highly exothermic- – please refer to the SAE Paper by DaimlerChrysler/Millennium that concentrated specifically on the relationship between the water and thermal balance of the system. The water acts as a heat sink that allowed us to passively cool the system and reject most of the heat as steam out of the tailpipe- even with this- the fuel cell will likely need a larger heat exchanger since it is being fed hot humidified hydrogen stream.

This issue has been briefly discussed at pages 13-14.

System Capacity vs. Material capacity – The necessity of separate container storage of waste fuel that severely reduces volumetric capacity – Proposed single volume exchange bladder tanks are feasible for several reasons:

o heat generation- the waste fuel returns to the tank just below 100C- this heat would conduct through the bladder into the fuel and cause premature generation of H2 in the fuel tank

o material compatibility – the extremely high ph (14) makes it difficult to find bladder materials that would remain pliable

o As mentioned- the solubility of the waste fuel is particularly poor- when the NaBO2 precipitates, it will form very hard crystal clumps that will cause severe abrasion with any moving/ pliable bladder material

These issues have been briefly discussed at pages 13-14.

Required Corrections

Purity of Hydrogen- Generally, the reaction does release pure H2, however almost all hydrolysis methods (liquid – powder steam etc) will produce highly humidified streams of H2- while this can be desirable for most PEM systems considered for automotive use, it must be accounted for in the downstream design of the fuel cell humidification system. If not designed properly- lines, valves etc could freeze.

This issue has been briefly discussed at pages 13-14.

System Capacity vs. material capacity- pg 2 line 52-55 The author only compares the gravimetric density of the NaBH4 Water material mix against the 9% gravimetric System target set by the DOE. The Doe target is a system target that includes all components of the tank from the fill line to the inlet of the fuel cell- this includes tank, hoses, tubes, wires, valves, sensors, controllers, heat exchangers, humidifiers etc- Realistically the best observed system capacity NabH4 is <3% G.D

This comment is true and that's why we have made the required modifications and highlighting. See for example pages 3 and 6.

Sodium borohydride hydrolysis as hydrogen generator: issues, state of the art and applicability upstream from a fuel cell

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Abstract

Today there is a consensus regarding the potential of $NaBH_4$ as a good candidate for hydrogen storage and release via hydrolysis reaction, especially for mobile, portable and niche applications. However as gone through in the present paper two mains issues, which are the most investigated throughout the open literature, still avoid $NaBH_4$ to be competitive. The first one is water handling. The second one is the catalytic material used to accelerate the hydrolysis reaction. Both issues are object of great attentions as that can be noticed throughout the open literature. This review presents and discusses the various strategies which were considered until now by many studies to manage water and to improve catalysts performances (reactivity and durability). Published studies show real improvements and much more efforts might lead to significant overhangs. Nevertheless the results show that we are still far from envisaging short-term commercialization.

Keywords

Hydrogen; Hydrogen storage; Sodium borohydride; Sodium tetrahydroborate; Fuel cell.

1. Introduction

The unanimous opinion is hydrogen (H_2) has a great potential as energy carrier, particularly as a fuel for fuel cell applications. Nevertheless in order that a H_2 economy develops, some significant issues have to be addressed. One of the drawbacks with H_2, which is also one of its main challenges, is related to its storage. Indeed today several ways for storing H_2 e.g. high pressure, liquid hydrogen, metallic and chemical hydrides, and so on, are being investigated but none of them reaches yet satisfactory storage capacities from an application point of view. Among the various possibilities, chemical hydrides like e.g. sodium borohydride (sodium tetrahydroborate, $NaBH_4$) are viewed as having great potentials thanks to their high gravimetric/volumetric hydrogen storage capacities [1-3].

$NaBH_4$ (for its physical and chemical properties, see references [2,4-11]) is a well known chemical because it is often used in e.g. organic chemistry as reducing agent. $NaBH_4$ as a hydrogen storage material has a 60-year-old history, which has interestingly been reported briefly by Wee et al. [12,13] and at length by Demirci and Miele [14]. Discovered in the 1940s [15], its potential as hydrogen releasing material was remarked by the U.S. Army [10] and soon drew scientist's attention. However it was given up for a while from the middle of the 1960s. Recently, that is in the late 1990s, it met a new interest [16,17]. Amendola et al. [17] drew up a list of $NaBH_4$ advantages, amongst them we can cite e.g. non flammability of $NaBH_4$ solutions, stability in air for months, stability of reaction by-products which are environmentally safe and can be recycled. Though a prototype based on $NaBH_4$ hydrolysis has been constructed [16,17], H_2 generation through this reaction does not appear mature enough. Several issues like e.g. water handling, catalyst reactivity and deactivation, treatment of by-products and so on [12], hinder its development and do not permit to reach e.g. gravimetric hydrogen storage capacity (GHSC) that is satisfactory for an application point of view. Actually it is important to note here that the US Department of Energy has recommended no-go for the aqueous solution of sodium borohydride as a hydrogen storage solution for on-board vehicular hydrogen storage. We would like to emphasise that this recommendation has not envisaged storage for portable devices and storage ways alternative to the aqueous solution.

Hydrogen stored in $NaBH_4$ must be recovered either by thermolysis [14,18] or by hydrolysis [12]:

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

The latter reaction is much more investigated for several reasons, especially three. First, the hydrolysis of $NaBH_4$ is a spontaneous [19,20], exothermic reaction (-210 kJ mol^{-1} [21]) that besides can be accelerated thanks to a well chosen metal-based catalyst. Second, pure H_2 [21] can then even be produced at low temperatures (0-20 °C). Third, the fuel $NaBH_4$-H_2O stores 10.8 wt% of hydrogen and H_2O provides half of the H_2 [23]. However this reaction shows different hurdles. The first of them is both low solubility of $NaBH_4$ and solvation of sodium metaborate ($NaBO_2$) as by-product which implies that an important amount of water is needed to conduct the reaction. A second one is linked to the slow reaction rate. Indeed for practical reasons (e.g. storage) NaOH is added to the solution of $NaBH_4$ to slow down the self-hydrolysis which occurs when water is added to $NaBH_4$. Therefore an efficient catalyst is needed to decrease the activation energy and to accelerate the hydrogen generation rate (HGR). Both hurdles are the most studied ones as that can be remarked throughout the open literature.

In the next sections we propose to list and to discuss the strategies used to overcome these two main challenges. Note that there are other issues regarding the hydrolysis reaction: e.g. $NaBH_4$ production process which is expensive and $NaBO_2$ recycle [12,24,25]. More general reviews are available throughout the open literature. Wee et al. [12] discussed the latest research (till 2005) on the use of H_2 generated via $NaBH_4$ hydrolysis and listed the advantageous features of this reaction. More recently, Demirci [26] reported basics and advantages of $NaBH_4$ as hydrogen carrier. Çakanyıldırım and Gürü [25] reviewed the production of $NaBH_4$, more briefly its dehydrogenation and the $NaBO_2$ recycle. Anyway, some other issues are briefly tackled in the last section of the paper. To summary, the present review focuses the water handling challenge as well as the catalytic materials challenge because they are the most studied ones.

Prior to any discussion, it is very important to highlight a fundamental point. The storage capacity of $NaBH_4$ or system $NaBH_4$-H_2O is mostly discussed on the basis of the GHSC (wt%). However, there is a mistake that is often made throughout the open literature. The GHSC is generally calculated on the basis of only $NaBH_4$ and H_2O while this must be done on the basis of the complete storage system (including the tank, storage media, safety system, valves, regulators, piping, and so on). Indeed the GHSC is a system target. It is therefore to note that the following discussion tackles the GHSC as it is throughout the open literature (i.e. on the basis of $NaBH_4$-H_2O) while keeping in mind that they are overestimated.

2. Water handling challenge

From a theoretical point of view hydrolysis of 1 mole of $NaBH_4$ requires only two moles of H_2O:

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

but in real conditions the reaction needs more water to release 4 moles of hydrogen and can be written as :

$$NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O + 4\ H_2$$

with x the excess of water. Two reasons justify the utilization of an excess of water during $NaBH_4$ hydrolysis (Figure 1). The most important one is linked to $NaBH_4$ solubility in water. As reported by Kojima et al. [27], the $NaBH_4$ solubility at 25 °C is 55 g per 100 g water [28] or 1.46 mol per 5.56 mol. Accordingly the GHSC of such a fuel is 7.5 wt% (whereas 10.8 wt% with $x = 0$). However Kojima et al. [27] added that since the solubility of the by-product $NaBO_2$ is 28 g per 100 g water, the $NaBH_4$ concentration at 25 °C should be below 16 g per 100 g water to keep the liquid state of $NaBO_2$, which precipitation could cause losses in the catalytic performances. In that case the GHSC of the fuel is 2.9 wt%. This value is much lower than the claimed 10-20 wt% of most of the chemical hydrides [1].

The second reason justifying the excess of water is the fact that the stable form of the reaction by-product $NaBO_2$ is its hydrated form ($NaBO_2.xH_2O$) [25]. Figure 2 shows the evolution of the GHSC of the fuel $NaBH_4+(2+x)H_2O$ with the excess of water x. With $x > 3$, the GHSC is below 6 wt%, and this value is a criterion for 2010 settled by the U.S. Department of Energy (DOE) for automotive applications [29]. Beyond year 2015, it is expected capacities > 9 wt%, which excludes any excess of water ($x = 0$). Çakanyildirim and Gürü [25] has reported that a value of $x = 0.84$ should be enough to achieve a capacity of 9 wt%. However, as already noticed above, the values 6 and 9 wt% are system targets that includes all components of the complete storage system. Accordingly the system capacity of $NaBH_4$ is realistically < 3 wt% when $x > 3$ and 4.5 wt% when $x = 0.84$.

How reducing x, *i.e.* how optimising the GHSC of the fuel $NaBH_4+(2+x)H_2O$ is thus one of the main objectives of the different studies conducted. The next sections draw up and discuss the different alternatives which are studied to handle this problem.

2.1. Optimisation of the molar ratio $H_2O/NaBH_4$ of aqueous solutions

The first studies reporting hydrogen release capacities of $NaBH_4$ envisaged a hydrolysis reaction with a high $H_2O/NaBH_4$ molar ratio. For example, Schlesinger et al. [15] used an aqueous solution with a molar ratio $H_2O/NaBH_4$ of 42 (i.e. GHSC < 2 wt%). Among the most recent articles, Amendola et al.'s [16], reported a lower ratio but still higher than the ideal $x = 0$, that is a ratio of about 7 (i.e. GHSC = 4.2 wt%, stabiliser weight being taken into account). Xu et al. [30] suggested that in the viewpoint of practical application a $NaBH_4$ concentration of 15 wt% should be set in order to keep the by-product solution state and get relatively high hydrogen storage efficiency. However in such conditions the GHSC can only reach 3.2 wt%. Shang et al. [31] addressed the water excess issue through thermodynamic modelling. The optimal concentration of $NaBH_4$ was calculated while taking into account both possible precipitation of $NaBO_2$ and NaOH addition. It was showed that the maximum GHSC of the system $NaBH_4$-NaOH-H_2O is 2.2 wt% at 20 °C, which corresponds to a NaOH concentration of 0 wt%. The capacity decreases with increasing the NaOH concentration. At 80 °C, the maximum capacity is 5.1 wt% (with 0 wt% NaOH). On the other hand, Liu et al. [32] investigated thermal properties of $NaBH_4$-NaOH-H_2O. Firstly it was showed that it is possible to store and use the $NaBH_4$ solution below 0 °C if the NaOH concentration is less than 20 wt%. Secondarily the optimum composition for stabilising the $NaBH_4$ solution is 15 wt% $NaBH_4$ in 10 wt% NaOH considering both liquidus temperature and GHSC. This composition fits a GHSC of 3.2 wt%.

Another solution, maybe the most obvious, is to optimise the features of the hydrolysis reaction medium by decreasing the water content to a minimum. Hua et al. [33] showed that a GHSC of 6.7 wt% could be reached at room temperature with about 90 % of $NaBH_4$ conversion efficiency. In the experimental conditions 10 g of $NaBH_4$ was added to 18 g of H_2O, which is the solubility of $NaBH_4$ at 25 °C. It was noticed that considering the lower solubility of $NaBO_2$ and its stronger association with H_2O at lower temperature, small consumption of $NaBH_4$ should be expected. In addition, one may wonder about catalytic material durability because of possible $NaBO_2$ precipitation which can deactivate the catalyst. Such deterioration could lead to small conversion of $NaBH_4$ as well as lower HGR.

Although efforts were done to optimize the $H_2O/NaBH_4$ molar ratio the $NaBH_4$ solubility still prevents a satisfactory GHSC. This is one of the technical arguments that motivated the experts of DOE to recommend no-go for aqueous $NaBH_4$ solution [29]. Nevertheless, to by-pass the problem of $NaBH_4$ solubility, different studies envisaged to use $NaBH_4$ in a state which is different from aqueous solution. It is what we propose to describe below.

2.2. Utilization of $NaBH_4$ under various forms

2.2.1. Powder

The utilization of $NaBH_4$ powder is not a new idea. It was first introduced by Kong et al. [34] who studied H_2 generation from various hydrides. In that case water vapour is used instead of liquid water. The idea is basically to store solid $NaBH_4$ while H_2O vapour is recovered from a fuel cell. Accordingly the GHSC would be 21.3 wt% (the weight of H_2O vapour is not considered in the calculation because it is supposed to be generated in a fuel cell and so not stored anywhere). However Kong et al. [34] observed that $NaBH_4$ did not react with H_2O vapour. Despite this failure, the idea of using solid $NaBH_4$ was considered one more time. Marrero-Alfonso et al. [35,36] reported that the reaction of $NaBH_4$ with steam produced H_2 and a hydrated solid, and that up to 95% yield of H_2

was obtained with pure steam without any catalyst. Thermogravimetry and X-Ray Diffraction analysis revealed that the solid by-product was a hydrated borate corresponding to $NaBO_2.2H_2O$. The dihydrate form of $NaBO_2$ is the stable form at temperatures up to 105 °C and the degree of hydration of the product is not a direct function of water/hydride ratio originally present in the system [36]. According to Kong et al. [34], 21.3 wt% is the highest hydrogen density if only $NaBH_4$ is considered as being initially stored in the case of an on-board application (Figure 3). Can this ideal value be reached when $NaBO_2.2H_2O$ is the reaction product? In order to attempt to answer this question, let us consider an example. For an on-board application the weight of the stored contents in the tank is crucial (the volume is not regarded) and thus the hydrated by-product weight is the limiting factor. If the up-limit of the tank is 1000 g, this one will only store 1000 g of $NaBO_2.2H_2O$ or, initially, 371 g of $NaBH_4$ (supposing equivalent the densities of both reactant and by-product). Accordingly the effective $NaBH_4$ GHSC of the tank will only represent 37 % of its maximum capacity. Now if one supposes that 1000 g of $NaBH_4$ is equivalent to a GHSC of 21.3 wt%, 371 g of $NaBH_4$ will be equivalent to 7.9 wt%. Note that if the reaction by-product is anhydrous $NaBO_2$, the effective capacity will be equivalent to 12.2 wt%. This trivial calculation illustrates the issues due to the formation of stable hydrated by-products. Marrero-Alfonso et al. [36] wrote that the fact that $NaBO_2.2H_2O$ appears to be a favoured product will complicate the process design. We agree. Another example of complication which could be a limited or hindered diffusion of water vapour through a superficial layer of hydrated $NaBO_2$. This possible issue was also suggested by Çakanyıldırım and Gürü [25]. A solution can be a stirring system, which mixes the whole solid for dragging the reaction by-products far from the water inlet. However that may be, the idea of using H_2O vapour is good but this one has not been developed yet. With the deepening of the studies and with the benefit of hindsight, the system might be improved and optimised, knowing that every improvement should permit to reach effective GHSC above the specification 9 wt%, the ideal limit being none other than 21.3 wt%. Furthermore no catalyst has been added to solid $NaBH_4$ yet.

Another solution which could be envisaged is to use stoichiometric proportions of liquid water and solid $NaBH_4$. This is what Kojima et al. [37] applied. They observed that by increasing the pressure, the hydrogen yield is twice better. They introduced the catalyst ($Pt-LiCoO_2$) mixed with $NaBH_4$ in a closed pressure vessel and then a stoichiometric amount of H_2O was injected. The GHSC (including the catalyst) was 9.0 wt%. From our calculations based on the values given by Kojima et al. [37] (i.e. catalyst/$NaBH_4$ = 0.2 g/1 g), the maximum GHSC was 9.8 wt%. The GHSC that was reached by this process is outstanding because it is high enough to reach the DOE targets for automotive applications. However such hydrolysis system induces some questions, especially from practical point of view. Will all of the generable H_2 be produced in one time? Or will it be possible to use this system during transition stages (go-and-stop)? If generated H_2 is immediately consumed by a fuel cell the H_2 pressure could not increase anymore and in that case will the GHSC of 9.0 wt% be reached? What was the hydration degree of $NaBO_2$? Is there any dependence between $NaBO_2$ hydration degree and H_2 pressure? In fact, all of these questions can be grouped together in a single one: is 9.0 wt% reachable in fuel cell vehicle application? Recently, Liu et al. [38] published a work that is slightly different from Kojima et al.'s [37]. The main difference with Kojima study relies on non-pressurized system. Hydrogen could be liberated at very high rates ($CoCl_2$-catalysed), such as over than 90 % conversion rates were achieved. Final H_2 generation capacity was achieved as high as 6.7 wt%. This study is actually quite similar to Hua et al.'s [33] even if in their conception they are different since the former used the reactant in its solid form while the latter used an aqueous solution. In both studies, the molar ratio of H_2O to $NaBH_4$ was about 4 and the same GHSC were reached, i.e. 6.7 wt%. Accordingly, the advantage of using solid $NaBH_4$ is not so obvious. Water diffusion onto the catalytic surface for the solid system should be much more limited and difficult than for an aqueous solution. In fact, a comparative study of both configurations lacks. Cento et al. [39] also considered solid $NaBH_4$ but they mixed it together with the catalyst (salt of Ni or of Fe). Excess of water was then added to the mixture to start the hydrolysis reaction. Today the investigations are in their early stages but there is no doubt that new results and findings will be soon published.

2.2.2. *Gel*

Recently, Liu et al. [40] reported an original, innovative solution. A sodium polyacrylate was used as super absorbent polymer (it can absorb water, as much as 200–800 times its own mass) to form alkaline $NaBH_4$ gel and explored its possibilities for $NaBH_4$ hydrolysis. It was found that the absorption capacity of sodium polyacrylate decreased with increasing $NaBH_4$ concentration. For example, for a stabilised (5 wt% NaOH) solution at 25 wt% of $NaBH_4$ the polymer was able to adsorb at about 5 times in weight, what corresponds to a GHSC of 4.5 wt% (but the amount of catalyst is not taken into account). H_2 generation from the gel was carried out using $CoCl_2$ catalyst precursor solutions. It was higher than that obtained from an alkaline solution. Typical experimental conditions were 30 g of gel and 15.2 g of $CoCl_2$ solution, what implies a GHSC of about 3 wt%. The idea of using an adsorbent is good but the preliminary results must be developed in order to reach higher GHSCs. Optimisations (e.g. modified polymer, optimised solution, addition of additive, and so on) may again improve the capacities. Furthermore, using such storage system can solve application issues. For example, Liu et al. [45] reported that with the $NaBH_4$ gel power generation devices can be placed in all directions without preference and can avoid impurities like $NaBH_4$, $NaBO_2$ and NaOH. It was besides reported that borohydride ions diffuse in alkaline gel particles quicker than in alkaline solution. Furthermore, in our opinion the polymer could be a potential support for a metal catalyst like e.g. cobalt or cobalt boride, the polymer having then a double role, which is to store both $NaBH_4$ and H_2O and to support the catalytic material. Nevertheless questions arise. Is the polymer stable enough to suffer the alkalinity of the borohydride solution as well as the presence of catalyst? What is the gel behaviour when $NaBO_2$ precipitates since it solubility is well below that of $NaBH_4$?

To conclude, it can be remarked that the highest GHSC (Figure 3) that might be reached by using $NaBH_4$ gel is 7.5 wt% (for 55 g of $NaBH_4$ per 100 g of H_2O, the solubility of $NaBO_2$ and the amount of NaOH being not taken into account). For some portable applications, this storage system could be the ideal solution. The idea of using a matrix (e.g. polymer) for storing $NaBH_4$ and/or H_2O and/or catalyst must be further developed.

2.2.3. *Methanolysis as an alternative of hydrolysis?*

There are generally two ways to face an issue. The first one is to try to optimize of the experimental conditions as reported in the previous sub-sections. The second way is simply to by-pass the problem by changing the experimental approach. The latter way is what Lo et al. [41] chose to do. To avoid the formation of the hydrated reaction product, an alternative to H_2O utilization as reactant is the use of a primary alcohol. Indeed $NaBH_4$ is known to be reactive to e.g. methanol and ethanol [42] and methanol has the highest reactivity toward $NaBH_4$ [41]. The overall reaction between methanol and $NaBH_4$ can be described as:

$$NaBH_4 + 4\ CH_3OH \rightarrow NaB(OCH_3)_4 + 4\ H_2$$

This system has a 4.9 wt% GHSC (Figure 3). Lo et al. [41] assessed the H_2 generation in methanol and mixtures of methanol and water ($H_2O/NaBH_4$ mole ratio of either 2 or 10). The best system was the mixture with a mole ratio of 10. However Lo et al. [41] recognised that methanolysis of $NaBH_4$ will not likely meet the DOE criterion of 9.0 wt% hydrogen storage system density for automotive fuel cells by 2015 as it is also the case for the base-stabilised hydrolysis. This is all the more true because the maximum GHSC is 4.9 wt%. It is thus impossible to increase this value.

Due to a maximum GHSC below 5 wt%, one can rightfully wonder about the interest of such a system based on the utilisation of methanol. What could be the advantage(s) of using methanol instead of water? Is it relevant to consider methanol as a potential fuel while it is known as being toxic (instead of safe water)? Is the methanolysis reaction product $NaB(OCH_3)_4$ recyclable? Or is it more easily recyclable than $NaBO_2$? If the methanolysis is metal-catalysed, should one expect the generation of secondary by-products like e.g. carbon monoxide and carbon dioxide? All of these questions perplex. Even the utilisation of methanol vapour will not improve the GHSC of 4.9 wt%.

The investigations about the system $NaBH_4$-CH_3OH are in their early stages. The utilisation of methanol may be viewed as a potential solution in order to avoid the problems due to the formation of hydrated by-products.

2.3. Summary

A GHSC of 10.8 wt% is attractive. $NaBH_4$ has this property but the effective capacities are unfortunately well below this ideal value for two main reasons: the use of water excess to lead $NaBH_4$ solubility and the hydration of the reaction by-product $NaBO_2$. Typically the first studies reported capacities < 2 wt%. To overcome the water excess issue, several solutions were proposed. These solutions permitted to improve the effective GHSCs. For example, with highly concentrated aqueous solutions capacities of about 7 wt% were obtained while with solid $NaBH_4$ capacities up to 9.0 wt% were observed. The thermodynamically stable form of

$NaBO_2$ is the dihydrated one [35,40], which means a maximum GHSC of 7.3 wt%. For obtaining higher capacities, the $NaBO_2$ hydration issue should be addressed.

In less than 10 years the effective GHSCs have improved reaching values closer to the ideal capacity. Even if for some of the proposed solutions the maximum own effective GHSC appears to be reached, for others and especially for the storage of solid $NaBH_4$, H_2O being provided as vapour, capacities up to 21 wt% could ideally be obtained.

However, it is here important to note one more time that the discussed GHSCs are only based on $NaBH_4$ and H_2O. If one now considers the complete storage system, it is evident that the values that have been experimentally evidenced fall short of the targets set for automotive applications. For example, if one arbitrarily supposes that the components of a storage system weigh 50% of the total weight, the GHSCs listed above should be divided by a factor of 2. And, the highest GHSC that might be expected is 10.8/2, namely 5.4 wt%. Such value confirms that $NaBH_4$ cannot be considered for automobile applications but it still has a potential for mobile, portable and niche applications.

Throughout the present section as well as in the papers cited here, the volumetric hydrogen storage capacity (VHSC) has never been tackled. It is generally not taken into account because of two main reasons. First, the hydrolysis is in most cases performed in diluted solution, which strongly penalizes the VHSC. Second, since the GHSC falls short of the application targets, the VHSC is even not considered. However that may be, the VHSC is as important as the GHSC.

Stored hydrogen has to be generated for fuelling fuel cell. The HGR is then a critical parameter since it will depend on the power of the fuel cell. This means that the production should be efficient enough to permit variable HGRs and maximum yields. This is the role of the catalyst.

3. Catalytic materials challenge

H_2 can be released spontaneously by self-hydrolysis [19,20,43]. It was reported that the rate at which $NaBH_4$ self-hydrolyses in water (without catalyst) depends on the pH and solution temperature [19]. The rate is empirically represented by

$$\log(t_{1/2}) = pH - (0.034T - 1.92)$$

with $t_{1/2}$ the time (min) it takes for one-half of a $NaBH_4$ mole to decompose versus temperature (K) [44]. To avoid the self-hydrolysis, due to the fact that such spontaneous reaction is undesirable from an application point of view, $NaBH_4$ aqueous solution is stabilised by making it alkaline through addition of sodium hydroxide (or eventually potassium hydroxide) [19]. For example, for pH 14 and at 25 °C (298 K), $NaBH_4$ solutions have a half-life time of 430 days [17]. Therefore catalysts must be used to accelerate H_2 generation by $NaBH_4$ hydrolysis. According to Wee et al. [12] the most important factor involved in the successful use of H_2 generated via $NaBH_4$ hydrolysis reaction is the preparation and development of optimum catalyst. As reported in this review catalysts used are exclusively transitions metal-based and are used in various forms: salt, bulk, nanoparticles, supported, and alloy (supported or not) [12].

The present section draws up the nature of these catalytic accelerators and discusses both their performances and their durability.

3.1. Catalysts nature

3.1.1. Acids

Utilization of acids to generate H_2 from $NaBH_4$ was studied mainly in the 1950-1960s. First, Schlesinger et al. [15] observed that the hydrolysis reaction was greatly accelerated by addition of acidic substances. In their study a large number of acids were tested like e.g. oxalic acid, citric acid or boric oxide. Then several papers reported fundamental studies determining e.g. the kinetics and the reaction mechanisms of the acid-catalysed hydrolysis of $NaBH_4$ [45-49]. Today acids are not investigated anymore. It appears that they are not regarded as potential accelerators and in our opinion it is regrettable. For example, when solid $NaBH_4$ is stored, H_2O is supposed to be provided to start the H_2 generation. An acid solution might be as efficient as either a metal salt solution or a supported metal. Furthermore issues related to safety, catalyst recovery and recycling, cartridge/tank design might be (partially) solved. Acids have thus a potential.

3.1.2. *Metallic salts*

Today catalysts used are metal-based materials. The first metal-based materials used are metal salts (Table 1) [15,38,50,51]. Schlesinger et al. [15] had tested manganese, iron, cobalt, nickel and copper chlorides. They reported that particularly striking was the catalytic effect of certain metal salts, especially that of cobalt chloride. The kinetics of cobalt chloride-catalysed hydrolysis was studied and a first-order reaction with respect to the $NaBH_4$ concentration and activation energies of 17.5 to 29.5 kcal mol^{-1} depending on the sodium borohydride concentration were reported [52]. Later Brown and Brown [50] screened much more metal salts (Table 1), especially noble metal-based salts. Platinum was a highly effective catalyst, more effective than cobalt. Both ruthenium and rhodium were more active catalysts but palladium exhibited much poorer catalytic activity. Kaufman and Sen [49] investigated various salts based on the same metals than those studied by Schlesinger et al. [15]. It was especially found that the catalytic activity of the metal salts was dependent on the cation (Co^{2+}, Cu^{2+} and Ni^{2+}) while it was independent of the anion (Cl^-, NO_3^- and $CH_3CO_2^-$). Recently Liu et al. [51] compared cobalt chloride, nickel chloride and for the first time nickel fluoride. The highest reactivity of the cobalt salt was confirmed but the HGR was much lower than the rates obtained in references [15,50]. This may be explained by the fact that Liu et al. [51] stabilised the aqueous solution with 10 wt% NaOH. The nickel fluoride was 3 times more reactive than the nickel chloride but it was much less reactive than cobalt chloride this does not make it a suitable catalytic material. Liu et al. [38] reported HGRs of about 11 L(H_2) min^{-1} g^{-1}(Co) for cobalt chloride and gravimetric hydrogen storages up to 6 to 7 wt% ($NaBH_4$ was stored as solid and aqueous solution cobalt chloride was added). To our knowledge, this performance is likely the best ever reported for the cobalt chloride salt.

Table 1 list the performances of the metal salts tested. Obviously the noble metal-based salts are the most reactive ($RuCl_3$, $RhCl_3$ > H_2PtCl_6). They are followed by cobalt chloride, which appears to be a promising alternative to noble metals because it is reactive while being cheaper. This explains why most of the published papers deal with the improvement of the cobalt-based catalysts reactivity (see the next sub-sections). However Schlesinger et al. [15] reported that the effect of the cobalt salt is ascribed to the catalytic action of cobalt boride Co_2B, which is formed in the initial stages of the reaction. Typically it was observed that the salts reacted rapidly with $NaBH_4$ solutions and gave finely-divided black precipitates [15,50]. According to Schlesinger et al. [15] the precipitates were probably borides. According to Brown and Brown [50], the precipitates were the noble metals (e.g. platinum) reduced to the elementary state. In both cases, it was remarked that the precipitates were active, effective catalysts for the hydrolysis of $NaBH_4$. Therefore Schlesinger et al. [15] and Brown and Brown [50] considered that the active catalysts were cobalt boride and platinum (0), respectively. Accordingly metal borides like e.g. cobalt or nickel borides are today much investigated (discussed in the next sub-section).

3.1.3. *Metal borides*

Cobalt boride has drawn a particular attention to itself. Jeong et al. [53], Wu et al. [54] and Walter et al. [55] prepared cobalt boride by the chemical reduction method using $NaBH_4$ as a reduction chemical. This method is in fact the most common for obtaining metal borides. In addition, Wu et al. [54] heat-treated the obtained CoB at various temperatures. It was observed that the catalyst treated at 500 °C exhibited the best catalytic activity because it had the best crystallisation (the more crystallised, the more active). This material achieved an average HGR of about 3 L(H_2) min^{-1} g^{-1}(CoB). According to Wu et al. [54], this rate may give a successive H_2 supply for a 481 W PEMFC at 100 % H_2 utilisation. Liu et al. [51] compared the catalytic activity of Co_2B to that of cobalt powder, cobalt chloride and Raney cobalt. Co_2B (468 mL(H_2) min^{-1} g^{-1} (Co_2B)) was better than the powder (126 mL(H_2) min^{-1} g^{-1}(Co)) and the Raney (268 mL(H_2) min^{-1} g^{-1} (Co)) but was less active than the chloride (570 mL(H_2) min^{-1} g^{-1}(Co_2B)). Patel et al. [56,57] used CoB-based thin film catalyst synthesised by pulsed laser deposition technique which permitted the formation of CoB nanoparticles. It was observed that cobalt was efficient only when alloyed with boron which partially prevents metal oxidation.

Modified CoB-based catalysts were besides investigated. Ingersoll et al. [58] reported nickel-cobalt-boride NiCoB (molar ration Ni:Co of 1:1) that were prepared by the chemical reduction method. Nickel is also a metal which boride-based compounds were also studied. For example, Walter et al. [55] observed a maximum HGR of 1.3 L(H_2) min^{-1} g^{-1}(Ni_3B) for a Ni_3B catalyst. Hua et al. [33] claimed the preparation of a highly stable and active nickel boride catalyst (Ni_xB) even if its performance were four times lower than that of a Ru-based catalyst at room temperature. Ni_2B was tested by Liu et al. [51] but this catalyst was quite inefficient. Chen and Kim [59] synthesised nickel-boride-silica nanocomposites, the boride function being formed by the chemical reduction method using $NaBH_4$. At 25 °C, NiB-SiO_2 was three times less efficient than Pt-SiO_2.

A catalyst in powder form is not conceivable from an application point a view and that's why CoB was supported over a substrate, mainly nickel foam. Even if it is used as a substrate, catalyst-free Ni foam catalyses the hydrolysis of $NaBH_4$ [60]. Mitov et al. [61] electrodeposited CoB with Mn on nickel foam leading to CoMnB-Ni. Dai et al. [62] optimised an electroless plating method for the preparation of amorphous CoB catalyst supported on nickel foam (porous structure, low density, high thermal and chemical stability under the hydrolysis conditions). One of the highest HGRs was observed, i.e. 11 L(H_2) min^{-1} g^{-1}(CoB-Ni). In a further study, Dai et al. [62] modified the CoB-Ni catalyst by introducing a new element, that is, tungsten. The same electroless plating method was used. Via optimizing these preparation and reaction conditions, the CoWB-Ni material (87.0 wt% Co, 4.5 wt% W, 8.5 wt% B) achieved a HGR of 15 L(H_2) min^{-1} g^{-1}(CoWB-Ni). According to the authors, this rate is comparable to the highest level of noble metal catalyst. A CoB-Ni catalyst obtained by an electroless method was also reported by Krishnan et al. [63] but the performances were much less sharp. Liang et al. [64] suggested a new approach for optimising the catalytic ability of the catalyst: the modification of the nickel foam substrate. Cobalt boride supported over palladium modified nickel foam was prepared. It showed an average HGR of about 2.9 L(H_2) min^{-1} g^{-1}(CoB-PdNi). It was concluded that the presence of Pd has three advantages: it improves the catalysts stability; it increases the activity for H_2 generation because of its activity towards $NaBH_4$; and, it adsorbs and stores hydrogen during the process of H_2 generation.

Table 2 summarises the HGRs of the various metal borides discussed in the present section. It stands out that the most efficient material is CoWB-Ni [65] since it shows the best HGR (15 L(H_2) min^{-1} g^{-1}), the highest GHSC (4.2 wt%) and a maximum H_2 generation yield (100 %). This promising result shows that further improvements can be expected if the catalytic material, the hydrolysis medium and the hydrolysis conditions are further optimised. The great interest is that these materials must replace noble metals like e.g. Pt and Ru.

3.1.4. Reduced transition metals

Ruthenium is known to be the most reactive metal for hydrolysing $NaBH_4$. It has been used as catalytic accelerator of the prototype produced by Millenium Cell [16,17]. In that case, ruthenium as $RuCl_3$ was dispersed on an anionic exchange resin (acting as a substrate of the catalytic phase) and then reduced by addition of a solution of $NaBH_4$. However it is not clear whether the catalyst is either metallic Ru or ruthenium boride (Ru_2B). So in the present review paper it is supposed that ruthenium could be metallic. Walter et al. [55] also used ruthenium, the catalysts being obtained through the metal salt reduction. Özkar et al. [66,67] reported the use of ruthenium nanoclusters obtained from the reduction of $RuCl_3$ by $NaBH_4$ and stabilised by specific ligand (acetate ion). Recently Özkar et al. [68] employed ruthenium acetylacetonate but as homogeneous catalyst. After reaction this material was not reduced by $NaBH_4$ and remained unchanged.

Ruthenium is the most reactive metal but it is also the most expensive one. Hence it is essential to propose an alternate, cheaper, reactive metal. Liu et al. [51] tested cobalt and nickel in various states: fine metal powder, metal salt (see section 4.1.2), metal boride (see section 4.1.3) and Raney metal. In most cases cobalt showed higher catalytic activity than nickel but Raney Ni was as efficient as Raney Co. The tested Raney materials i.e. Ni, Co, $Ni_{25}Co_{75}$, $Ni_{50}Co_{50}$, $Ni_{75}Co_{25}$ were the most reactive ones. From density functional theory-based calculations, it is expected that Ni segregates at the surface when it is alloyed to Co and that the Co sites bind more strongly adsorbates [69]. Co should then be much more dispersed at the surface, what means much more Co active sites are available. This might be an explanation of the better reactivity of the Raney NiCo. Kim et al. [22,69] investigated filamentary nickel but the HGRs were of about 0.1 L(H_2) min^{-1} g^{-1}(Ni). Besides ruthenium, Özkar et al. [71] studied water-dispersible stabilized nickel nanoclusters, which according to the authors was a highly active catalyst even at room temperature.

Cobalt is maybe the most promising non-noble metal. With the objective to improve its reactivity, some studies worked on its modification. For instance Liu et al. [72] tried to fluorinate various metals (e.g. Ti, Mn, Fe, Co, Ni, Cu, Zn, Ru) in order to prevent the formation of oxide at the metal surface. Co-F showed the best performances but one can regret that no result for non-fluorinated Co is available to evaluate the real reactivity of CoF. Cho and Kwon [73] prepared Co-P catalysts electroplated on Cu (the pure Cu substrate was quite inactive towards $NaBH_4$ hydrolysis). It was observed that CoP-Cu (13 at% P) exhibited a catalytic activity 18 times higher than that of Co-P prepared in similar conditions. In a further study Cho et al. [74] prepared CoP-Cu by an electroless method and the optimised catalyst exhibited a HGR of 3.3 L(H_2) min^{-1} g^{-1}(CoP) at 30 °C, which was 60 times faster than that obtained with Co-Cu. Another way for improving the reactivity of Co was proposed by Malvadkar et al. [75] who prepared a nanoporous Co film by an oblique angle polymerization method using the nanostructured PPX-Cl film as a substrate. This material showed a promising performance with a HGR of 4.3 L(H_2) min^{-1} g^{-1}(Co) at room temperature.

Park et al. [76] investigated bimetallic and trimetallic alloys. Ru was chosen as a primary metal and e.g. Co, Ni, Fe, Ag, and Cu were chosen as secondary metals. HGRs of about 18.0 L(H_2) min^{-1} g^{-1}(metals) were observed for $Ru_{60}Co_{40}$ and $Ru_{80}Fe_{20}$ while the rate reported for Ru was of about 7.0 L(H_2) min^{-1} g^{-1}(Ru). The most efficient catalyst was $Ru_{60}Co_{20}Fe_{20}$ with a performance of 26.8 L(H_2) min^{-1} g^{-1}(metals).

The HGRs reported for the metals discussed above are summarised in Table 3. Compared to the metal salts (Table 1) and to some cobalt boride-based catalysts (Table 2), the metals do not show satisfactory performances. The highest rates are of about 27 L(H_2) min^{-1} g^{-1}(Ru,Co,Fe) [76] in a reaction medium storing 2.1 wt% of hydrogen. Actually besides the Park et al.'s work [76] the most promising study is Amendola et al.'s [16] since besides a HGR of 22 L(H_2) min^{-1} g^{-1} (Ru) obtained at 55 °C the GHSC was 4.2 wt%. Note that for most of the other metal catalysts, the GHSC was well below 1 wt%, often 0.1-0.2 wt%, and such values reveal experimental conditions that were rather favourable for reaching good catalytic reactivities. Reduced metal materials do not appear as being potential catalysts for accelerating the H_2 generation. Accordingly supported metals have been investigated in order that the support improves the metal reactivity.

3.1.5. Supported metals

Supporting an active phase like a transition metal is generally a good way for reducing the amount of metal while maintaining or even improving its reactivity. A support may have a geometric effect (e.g. dispersion of the metal) and/or an electronic effect (change in the electronic environment of the metal), what ideally improve the metals reactivity and/or durability.

Regarding the hydrolysis of $NaBH_4$, Kojima et al. [27] reported the first study dealing with supported transition metals. Various oxides as support (Co_3O_4, TiO_2, SiO_2, NiO, $LiMn_2O_4$, TiO, CoO, Ti_2O_3, $LiNiO_3$, $LiCoO_2$) and supported Fe, Ni, Pd, Ru, Rh and Pt catalysts were first screened. The 1.5 wt% Pt-$LiCoO_2$ catalyst showed the best performances. A HGR higher than 200 L(H_2) min^{-1} g^{-1} (Pt) was observed and it was stressed that this rate was 10 times faster than the Ru catalyst reported by Amendola et al. [16]. It was suggested that the lithium cobaltite ($LiCoO_2$) support adsorbs water that provides protons reacting with the hydrides of the borohydrides adsorbed over the Pt sites. In a further article, Kojima et al. [77] discussed the performance of testing of a hydrogen generator (gravimetric and volumetric hydrogen storage densities of 2 wt% and 1.5 kg H_2/100 L of $NaBH_4$ solution, respectively) using the Pt-$LiCoO_2$ catalyst that was coated over a honeycomb monolith. It was emphasised that for this storage system the volumetric density was similar to that of the compressed hydrogen at 25 MPa. From that moment, several research groups envisaged the utilisation of $LiCoO_2$. Krishnan et al. [78] alloyed Pt to Ru and compared 10 wt% PtRu-$LiCoO_2$ to both 10 wt% Ru-$LiCoO_2$ and 10 wt% Pt-$LiCoO_2$. The efficiency of PtRu-$LiCoO_2$ was almost double of that of the Ru- and Pt-based catalysts. Few years later, Krishnan et al. [79] tested various supports for dispersing PtRu: e.g. Co_3O_4, NiO, $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, TiO_2, ZrO_2. The best catalytic systems were PtRu-Co_3O_4 followed by PtRu-$LiCoO_2$. The superior reactivity of these supports was attributed to the formation of CoB in the presence of $NaBH_4$. Furthermore it was suggested that the formation of catalytically active CoB from $LiCoO_2$ was slower than that from Co_3O_4, what explained the highest performance of the latter support. The formation of cobalt boride from $LiCoO_2$ and Co_3O_4 was also noted by Simagina et al. [80], who reported a HGR of 4.0 L(H_2) min^{-1} g^{-1}($LiCoO_2$) for the former support at 40 °C (without any metal as active phase). In fact after these promising performances, $LiCoO_2$ was often used as support [80-83]. Table 4 shows the HGRs of the $LiCoO_2$-based supported metals.

Otherwise many other supports were used for dispersing e.g. Co, Ru, Rh, Pd or Pt: C [30,33,76,83-90], C nanotubes [91], γAl_2O_3 [30,84,87,88,92], SiO_2 [27], TiO [27], TiO_2 [27,87,88,93,94], Ti_2O_3 [27], $LiMn_2O_4$ [27], CoO [27], NiO [27], $LiNiO_3$ [27], ZrO_2 [93], ZrO_2-SO_4^{2-} [89,95].

Table 5 and Table 6 report the best performances of C- and metal oxide-based (mainly γ-Al_2O_3 and TiO_2) catalysts, respectively. Globally the papers cited here screened various supports without attempting to deeply explain the positive or negative bringing of the supports. For example, Wu et al. [83] compared three C supports with different specific surface areas (i.e. 170, 823 and 1196 m^2 g^{-1}) and observed that the specific surface area was not the crucial factor. However no hypothesis was suggested. It seems that in this case the geometric effects of the supports on the metal are negligible and the reactivity might be explained by likely electronic effects. Furthermore it would have been interesting to have information about the acidity of the supports. The C support has often competed with γAl_2O_3. Xu et al. [84] suggested that the higher catalytic activity of Pt-C in relation to that of Pt-γAl_2O_3 was due to the large specific surface area of the latter support (i.e. 1055 vs. 248 $m^2 g^{-1}$). Such observation was also reported by Simagina et al. [87] since it was showed that whatever the metal the activity of Pt, Rh, Ru, and Pd metals supported onto C (530 $m^2 g^{-1}$), γAl_2O_3 (170 $m^2 g^{-1}$) and TiO_2 (243 $m^2 g^{-1}$) decreased in the order $TiO_2 > C > \gamma Al_2O_3$. This ranking was then confirmed for Rh supported catalysts [88]. It was suggested that electronic effects could explain this ranking and that the rhodium chloride interaction with TiO_2 determined the reactivity of rhodium particles formed under action of $NaBH_4$ medium. On the other hand, whatever the support, the activity of these catalysts decreased in the order Rh > Pt = Ru >> Pd [87]. On the opposite, Xu et al. [30] found that Co-γAl_2O_3 was more effective than Co-C. Data about e.g. the acidity of the support, the redox properties of the catalyst (both metal and support), and the electronic structure of the metal could have been useful in order to attempt to explain such variations. Even if one has to recognise that the investigations are in an exploratory stage, one may regret that much more fundamental analyses were not performed.

Another way for improving the catalytic performances of a supported catalyst is to alloy the active metal with another one. For example, as already discussed above in this section Krishnan et al. [78] found that alloying Pt to Ru (with $LiCoO_2$ as support) led to a more efficient catalyst than Pt- or Ru-$LiCoO_2$. When alloyed to Pt, Ru should strongly antisegregate, what means that much more small Ru sites should be dispersed on the surface [69]. Moreover Ru should bind more strongly the adsorbate, i.e. borohydride, what could activate more easily the H_2 generation [69]. In other words, an electronic effect as well as a geometric effect could improve the reactivity. The Hammer and Nørskov's [69] density functional theory-based predictions give a possible explanation of the enhanced reactivity of the PtRu alloy with respect to the single metals. The PtRu alloying was also assessed for the support Co_3O_4 [79]. Demirci and Garin [93,94] also adopted such a strategy in order to improve the efficiency of their Pt-TiO_2 and Ru-TiO_2 catalysts, respectively. In fact Demirci and Garin [93,94] used density functional theory-based results available in references [69,96] in order to establish a list of alloys to be tested. RuCu, RuPd, RuAg and RuPt, all supported over TiO_2, were selected. For these alloys, it was expected that the Ru particles, which aggregate at the surface, are smaller and better dispersed than for a surface of pure Ru [69,94]. Furthermore the adsorption on the Ru sites of the alloys was expected to be higher [69]. However in both studies [93,94] the addition of a second metal to either Pt or Ru was either detrimental or inefficient. For example, Ru was alloyed to Cu, Pd, Ag and Pt (atomic ratio 1:1 or for RuPt atomic ratios x:y of 2:1 or 1:2) and the activity decreased in the order Ru, Ru_2Pt_1 > RuPt, Ru_1Pt_2 > RuPd > RuAg, Pt > RuCu > PtAg [94]. Demirci and Garin [94] regretted therefore that the theoretical predictions from references [69,94] were unfortunately not confirmed in their experimental conditions. Park et al. [76] adopted a much larger strategy. A high throughput screening test was set in order to compare a number of metal alloy compositions. Since efficient unsupported alloys were obtained (as discussed in the section 4.1.4), Park et al. [76] supported some of the most efficient alloys over carbon fiber. While the HGR of unsupported $Ru_{60}Co_{20}Fe_{20}$ was 26.8 $L(H_2)\ min^{-1}\ g^{-1}$(Ru,Co,Fe), that of 16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-C was 41.7 $L(H_2)\ min^{-1}\ g^{-1}$(Ru,Co,Fe). This result showed the important role of the support in the reduction process leading to dispersed, small metal particles. Finally, carbon nanotubes supported PtPd catalyst was suggested by Peña-Alonso [91] but according to the authors the Pt and Pd atoms were apparently dispersed elementally. Table 7 proposes a list of the best rates ever reported for supported alloys.

Globally the HGRs reported in Tables 5, 6 and 7 were obtained in mild experimental conditions. Furthermore most of the catalysts reached rates well below 10 $L(H_2)\ min^{-1}\ g^{-1}$(metal). Compared to the $LiCoO_2$-based catalysts (Table 3), the C, γAl_2O_3, TiO_2 or ZrO_2 supported catalysts are much less reactive.

3.2. Catalysts performances

3.2.1. *Hydrogen generation rates*

Tables 1 to 7 report the performances of the catalysts discussed in the previous section. The list is certainly not exhaustive but the best performances ever reported throughout the literature are all listed. The best catalysts can be ranked thanks to the value of the HGRs that are given. However these values do not give an idea of the power levels that could be generated. Amendola et al. [16] suggested a trivial calculation for estimating achievable power levels from their hydrogen generator. It was assumed a standard PEMFC operating at 0.7 V. In that case, generating 1 g(H_2) min^{-1} should be equivalent to 1125 W (i.e. 26.8 A h × 60 min h^{-1} × 0.7 V × 1 min^{-1}). That is, 1 L(H_2) min^{-1} should power a 100 W fuel cell. This calculation can be used as a reference for estimating the power levels reachable for the best catalysts. Dai et al. [65] used this calculation and asserted that assuming a 100 % yield, a hydrogen generation system using 10 g CoWB supported on Ni foam could power a 15 kW PEMFC.

Table 8 reports the power levels reachable with 18 of the most reactive catalysts at temperatures from 20 to 30 °C. The best catalysts are defined as being the materials generating more than 1 L(H_2) min^{-1} g^{-1}(metal) from a system $NaBH_4$-NaOH-H_2O storing more than 2 wt% hydrogen. From Table 8, the main observation is that with 1 g of active metal powers from 100 W to 56 kW can be reached. These power levels are rather sufficient for powering mobile, portable applications (1 W to few kW) as well as bikes (250-500 W), scooters (500 W to few kW) and small cars (50-100 kW). Obviously with more catalyst higher power levels could be proportionally obtained. For example, 1 g or 10 g of CoWB supported on Ni foam can power a 1.5 or 15 kW PEMFC, what matches the Dai et al.'s [65] calculations. However for all of the catalysts reported in Table 8, the GHSCs fall short of e.g. the specifications for cars (i.e. 6 wt% for year 2010 and 9 wt% for 2015).

A second observation from Table 8 is that with the highly active catalysts like e.g. 10 wt% PtRu-$LiCoO_2$ only 2 mg of noble metals (or 20 mg of the catalyst) is sufficient for generating 100 W. This is a great, promising progress in reducing the cost of the catalyst. Less the noble metal amount is, cheaper the catalyst is.

From the performance point of view, there are obviously promising catalytic systems. However a highly efficient catalyst is otherwise a durable catalyst.

3.2.2. Long-life tests

Given the large number of studies published since the late 1990s, one has no choice but to admit that the efforts devoted to the catalysts have not really focused on the durability while the catalyst performance was the primary objective. The durability studies are actually quite new.

Kim et al. [70] tested the durability of a filamentary Ni catalyst over 200 cycles. It was observed that 76 % of the initial H_2 generation remained at 200 cycles. The main interest of this study is that the catalyst surface was analysed prior and after the cycling tests. Interestingly it was observed that the catalyst agglomerated, what brought about the diminishing of the catalyst specific surface area with cycling and so to the reduction of reactive sites. Furthermore it was observed that with cycling a film spreading the catalyst surface was formed. The deactivating film consisted of $Na_2B_4O_7.10H_2O$, potassium borate (KB_xO_y) and boron oxide (B_2O_3). It was thus concluded that the catalyst deactivation resulted was due to both agglomeration and film formed. Note that this study is certainly the most complete since at our knowledge none of the other papers dealing with durability reported such observations.

Özkar et al. [67,68,71] applied a procedure similar to that applied by Kim et al. [70] for testing the durability of their catalysts. At 25 °C and for a borohydride solution storing about 0.1 wt% hydrogen, Ru [67], Ni [71] and Ni [68] nanoclusters provided 5170, 1450 (over 240 min) and 1200 (over 180 min) total turnovers in the hydrolysis of $NaBH_4$ before deactivation, respectively. Chen and Kim [59], Dai et al. [65], Xu et al. [84], and Demirci and Garin [93,94] applied 3 to 6 cycles only for testing the durability of their respective catalysts. In each case, the catalyst showed a good durability. Whatever the experimental conditions in each study, it is obvious that the durability tests were too superficial. Aware of that, Xu et al. [84] emphasised that the stability of their Pt-C catalyst during long operating period for successive H_2 generation needs to be studied. One can agree while regretting the lack of such studies. Nevertheless in another paper Xu et al. [30] investigated the durability of Co-γAl_2O_3 in continuous flow conditions (1 mL min^{-1} of a 5 wt% $NaBH_4$ solution). Even if the GHSC of the fuel was only of 1.1 wt% and so the experimental conditions mild, there was no decrease in the catalytic activity during 330 min at constant flow rate. In these experimental conditions Co-γAl_2O_3 showed good durability to the hydrolysis of stabilised (5 wt% NaOH) $NaBH_4$ solution. Krishnan et al. [63] proposed a different approach. Extended operation was performed in a 1 L tubular reactor and CoB-Ni was tested in 10 wt% $NaBH_4$ solution for extended duration of up to 60 h. The H_2 generation decreased within 5 min and then it remained almost constant.

From a fundamental point of view, one can understand that in an early stage of investigations the durability tests are secondary. However from an application point of view the durability of the catalyst is as important as its reactivity. Accordingly the durability tests should be systematic and performed in much more severe testing/operating conditions.

3.2.3. *Catalyst shapes*

H_2 generation is expected to be controlled. That is, H_2 must be produced on demand. Depending on whether $NaBH_4$ is stored as solid, gel or aqueous solution the catalyst shape will be different.

If solid $NaBH_4$ is the chosen storage solution, the catalyst structure should not be the critical parameter for the H_2-controlled generation. The amount of water (liquid or vapour) should determine the H_2-controlled generation [35,36]. Using the catalyst either as a powder or supported over a substrate (resin, Ni foam, Cu plate, C cloth or paper, and so on) are two different solutions that can be envisaged. The final choice will depend on the final application.

If $NaBH_4$ gel is used [40], the catalyst has to be water soluble and to be provided with water. At this stage, it appears that the best catalytic solution is metal salt. Homogeneous catalyst may also be considered. Due to the fact that the background is not enough, it is difficult to suggest any other potential (soluble) catalysts. Powder catalysts or metal supported over a substrate do not seem suitable because it is expected that the catalytic site diffuses throughout the gel for catalysing stored $NaBH_4$.

Aqueous (stabilised) solution of $NaBH_4$ is the most investigated storage solution. The studied catalysts were regarded in various forms: powders, pellets and supported over a substrate. Using powder is practical from the one-shot experiment point of view because it is easy to design, to use in small amounts and to stir in aqueous solution. Many catalysts were tested as powder and such experiments permit to obtain reproducible HGRs. However it is difficult to recover, wash and re-use, and this is not practical for durability tests. Now if the application point of view prevails, it is difficult to imagine the utilisation of a powder catalyst. With such form, the go-and-stop utilisation is not conceivable. Indeed to start the hydrolysis of $NaBH_4$ the catalyst powder must be added into the aqueous solution but then it will be impossible to recover the powder catalyst in order to stop the H_2 generation. Actually the more practical option is the catalyst supported over a substrate. Amendola et al. [16,17] suggested the utilisation of a resin for dispersing Ru and such supported catalyst permitted the construction of a prototype. Another examples are the utilisations of either Ni foam for preparing supported cobalt borides [61,62] or Cu substrate for synthesising CoP [73,74]. Though no study deals with their utilisation, monolith and carbon cloth or paper could also be utilised. Note that interestingly Pozio et al. [97] suggested an original solution for utilising a catalyst as a powder. Nevertheless this solution has an inevitable condition. The powder must have iron-magnetic properties, since the reactor is constituted by a magnetic containment. With this prototype, the average hydrogen flow was 0.16 $L(H_2)\ min^{-1}$ during a working time of 15 h while fed with an 8 wt% $NaBH_4$ solution. As the Pozio et al.'s paper [97], several articles [98-101] reported the description of a hydrogen generator. Richardson et al. [99] remarked that the majority of the works utilised batch reactions and suggested an approach that is based on a flow reactor for continuous generation of H_2. Zhang et al. [100] reported a reactor design in which catalyst bed is integrated with a heat exchanger for autothermal operation. With this system, the integrated reactor performances were double than that of a simple reactor and 99 % of the $NaBH_4$ fuel was converted.

Whatever the way of storing $NaBH_4$ and whatever the way of bringing into contact $NaBH_4$ and H_2O, both know-how and engineering should provide solutions in order to bring into contact the catalyst with the system $NaBH_4$-H_2O and to control the H_2 generation. These solutions should make easy the go-and-stop process. In our opinion, there should be no doubt on that.

3.3. Summary

Regarding the efforts devoted to searching for outstanding metal-based catalysts, the global feeling is rather mixed. Whereas highly reactive catalysts have been found, their durability has unfortunately not been assessed. The best catalysts are actually able to generate H_2 at rates high enough for fuelling PEMFCs. However one cannot know if these catalysts can maintain their efficiency and, if they are durable one cannot know how long it will be efficient. The catalysts today investigated suffer from short-lifetime.

Another issue faced by catalysts is the material cost. There are two ways for reducing the material cost. The first is to reduce the content of the expensive, noble metal. The second is to replace the expensive metal by a cost-effective metal like for example Co. As shown in Table 8, the application of both possibilities led to synthesising reactive, less expensive catalysts. There is no doubt that further optimisations will lead to cheaper, active, efficient catalytic materials. Nevertheless a question arises. Which portion of the expense of the complete storage system does the catalyst cost represent? In other words, is the catalyst cost critical for this technology? Unfortunately to our knowledge there is no piece of information that permits to answer the questions.

The way of storing $NaBH_4$ should condition the catalyst shape. Given the state of the art and the current know-how, one may suppose that the catalyst form will not be an issue for implementing the technology.

4. Concluding remarks and other important challenges

4.1. General summary

$NaBH_4$ as hydrogen carrier is today far from being commercialised because it faces several issues. Nevertheless, only two of them are mainly reported throughout the $NaBH_4$-devoted literature. The first main issue is the effective GHSC of either $NaBH_4$ or the system $NaBH_4$-H_2O that is well below the ideal, theoretical value of 10.8 wt%. This issue led the DOE recommending no-go for the aqueous solution of $NaBH_4$ for on-board vehicle application. The second main issue is the efficiency of the catalyst in terms of durability.

Optimising the effective GHSC is intensely investigated (whereas the VHSC is rarely or even never studied). Besides the storage as an aqueous solution, several innovative, original solutions have been proposed: solid $NaBH_4$, $NaBH_4$ gel and utilisation of methanol instead of H_2O. Globally the solutions permitted to improve the effective GHSCs, reaching values up to 7-9 wt%. Capacities above 10 wt% could be reached with further improvements and optimisations. However the value 21 wt% seems somewhat surrealistic. Note that these GHSCs have been calculated only on the basis of the hydrogen carriers $NaBH_4$ and H_2O without taking into consideration the storage system as a whole. The GHSCs for a complete storage system should be much lower than the best values of 7-9 wt%.

A large number of catalysts (acids, metal salts, metal borides, metals, supported metals) were synthesised and assessed. Highly reactive catalysts have been found and these should be capable to generate H_2 for PEMFCs. In other words, one is today able to elaborate catalysts that permit to get adaptable HGRs. However there is today no information about the durability of these catalysts while the durability is a major criterion from an application point of view. Actually the catalysts, even the best ones, suffer from their short lifetime. Regarding the catalyst form, that should be a secondary or even a negligible issue.

4.2. Other challenges

The $NaBH_4$-based H_2 generator is not mature enough for fuelling PEMFCs. Further studies are required for optimising the GHSC and the catalyst efficiency especially in terms of durability. Moreover other important issues also hinder its development. These ones have not been discussed in the previous sections for the reasons evoked in the introduction but one can cite some of them that are in keeping with the chemical reaction $NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O + 4\ H_2$. For example, Amendola et al. [16] and Wee [12] emphasized it must be admitted that the commercial success of $NaBH_4$ will not be achievable without substantially reducing its cost, which is a significant issue. This has been one of the arguments against $NaBH_4$ when the no-go for automotive applications was announced [29]. One solution for reducing the cost of $NaBH_4$ could be the recycling of the reaction by-products but the recovering and the recycling of the metaborates is currently another significant issue [25]. Even though there are few articles reporting works about the borates recycling (see reviews under ref. [12,24,25]), an intense research within the framework of the DOE programs has been devoted to the recycle of $NaBO_2.xH_2O$ [102]. Such research involved several university groups and companies. Despite innovations, none of the investigated regeneration routes has met the targets in terms of regeneration efficiency, i.e. > 60 wt%, and cost. And the issue of recyclability seems to have played a central role in the no-go decision for the DOE [29]. As another example, one can cite the catalyst recycling issue that is rarely or even never taken into consideration.

The issues tackled in the previous paragraph are related to the catalyzed hydrolysis reaction. However, there are also issues that directly concern the technology from every angle, namely the storage system engineering [103]. Two examples are given hereafter:

- The $NaBH_4$ hydrolysis is highly exothermic and the heat must be managed [103,104]; in fact water acts as a heat sink and the humidified H_2 stream is then hot, which may be detrimental to the fuel cell [105]; moreover overly much water may be detrimental to the storage system if this one is not well designed (e.g. some components could freeze).

- The hydrolysis solid by-products have to be on-board stored till the conversion of all of $NaBH_4$; their storage can be envisaged in a separate bladder tank but several issues have then to be addressed: e.g. the heat of the waste fuel that can favour the $NaBH_4$ hydrolysis, compatibility of the bladder material with the highly basic (pH of 14) waste fuel, and the precipitation of $NaBO_2$ that forms hard crystal clumps that will cause severe abrasion with any pliable bladder material.

Anyway as a conclusion it could be written that further R&D efforts are necessary, at least for niche applications.

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Table 1. Performances of the metal salts.

Salt	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] L(H_2) min^{-1} g^{-1}	Reference
$MnCl_2$	25	1.0	< 49	< 1.2	[15]
$FeCl_2$	25	1.0	65	1.7	[15]
$FeCl_2$	25	0.4	50	1.2	[50]
$CoCl_2$	25	1.0	97	3.7	[15]
$CoCl_2$	25	0.4	50	4.9	[50]
$CoCl_2$	10	0.2	n.i. [d]	0.6	[51]
$CoCl_2$	20	6.8	92	11.4	[38]
$NiCl_2$	25	1.0	99	2.5	[15]
$NiCl_2$	25	0.4	50	2.5	[50]
$NiCl_2$	20	0.2	n.i. [d]	< 0.1	[51]
NiF_2	50	0.2	n.i. [d]	< 0.1	[51]
$CuCl_2$	25	1.0	49	1.2	[15]
$RuCl_3$	25	0.4	50	85.4	[50]
$RhCl_3$	25	0.4	50	85.4	[50]
$PdCl_2$	25	0.4	50	0.1	[50]
$IrCl_4$	25	0.4	50	0.5	[50]
H_2PtCl_6	25	0.4	50	13.3	[50]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in L(H_2) min^{-1} g^{-1}(metal).

[d] n.i.: not informed.

Table 2. Performances of the metal borides.

Boride	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
CoB	20	4.2	n.i. [d]	1.1	[53]
CoB	30	4.2	n.i. [d]	2.8	[53]
CoB	15	0.4	n.i. [d]	3.0	[54]
CoB	25	< 0.1	100	3.3	[56]
CoB	25	< 0.1	100	5.0	[57]
Co_2B	20	0.2	n.i. [d]	< 0.1	[51]
Co_3B	60	1.1	n.i. [d]	6.0	[55]
CoB-Ni	30	4.2	n.i. [d]	11.0	[62]
CoB-Ni	25	1.1	n.i. [d]	1.6	[63]
CoWB-Ni	30	4.2	100	15.0	[65]
CoMnB-Ni	20	1.1	n.i. [d]	n.i. [d]	[61]
NiCoB	28	0.7	100	2.6	[58]
Ni_2B	20	0.2	n.i. [d]	< 0.1	[53]
Ni_3B	60	2.1	n.i. [d]	1.3	[55]
Ni_xB	20	0.3	n.i. [d]	0.3	[33]
Ni_xB	20	0.3	n.i. [d]	0.8	[33]
NiB-SiO_2	25	0.1	n.i. [d]	2.2	[59]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(catalyst).

[d] n.i.: not informed.

Table 3. Performances of the transition and noble metal.

Metal	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] L(H_2) min^{-1} g^{-1}	Reference
Co powder	20	0.2	n.i. [d]	0.1	[51]
Raney Co	20	0.2	n.i. [d]	0.3	[51]
Co-F	25	n.i. [d]	n.i. [d]	0.4	[72]
CoP-Cu	30	2.1	n.i. [d]	1.0	[73]
CoP-Cu	30	2.1	n.i. [d]	3.3	[74]
Co-PPX-Cl	25	0.5	n.i. [d]	4.3	[75]
Ni powder	20	0.2	n.i. [d]	< 0.1	[51]
Filamentary Ni	30	3.3	n.i. [d]	0.1	[22]
Ni nanoclusters	25	0.1	n.i. [d]	1.7	[71]
Raney Ni	20	0.2	n.i. [d]	0.2	[51]
Raney $Ni_{25}Co_{75}$	20	0.2	n.i. [d]	1.5	[51]
Raney $Ni_{50}Co_{50}$	20	0.2	n.i. [d]	0.7	[51]
Raney $Ni_{75}Co_{25}$	20	0.2	n.i. [d]	1.2	[51]
Ru	25	4.2	n.i. [d]	4.0	[16]
Ru	55	4.2	n.i. [d]	22.0	[16]
Ru	60	1.1	n.i. [d]	18.6	[55]
Ru nanoclusters	25	0.1	70 [e]	2.7	[66]
Ru nanoclusters	25	0.1	70 [e]	1.0	[67]
Ru acetylacetonate	25	0.1	n.i. [d]	1.1	[68]
$Ru_{60}Co_{40}$	25	2.1	n.i. [d]	17.5	[76]
$Ru_{80}Fe_{20}$	25	2.1	n.i. [d]	18.3	[76]
$Ru_{60}Co_{20}Fe_{20}$	25	2.1	n.i. [d]	26.8	[76]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in L(H_2) min^{-1} g^{-1}(catalyst).

[d] n.i.: not informed.

[e] The reaction was ceased when 70 % conversion was achieved [66,67].

Table 4. Performances of the $LiCoO_2$ supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
1 wt% Ru-$LiCoO_2$	25	2.1	n.i. [d]	n.i. [d]	[77]
10 wt% Ru-$LiCoO_2$	25	2.1	n.i. [d]	428	[78]
1 wt% Rh-$LiCoO_2$	40	0.5	n.i. [d]	122	[80]
1 wt% Pt-$LiCoO_2$	25	2.1	n.i. [d]	n.i. [d]	[82]
1.5 wt% Pt-$LiCoO_2$	22	4.2	100	203	[27]
10 wt% Pt-$LiCoO_2$	25	2.1	n.i. [d]	300	[78]
15 wt% Pt-$LiCoO_2$	20	0.1	95	367	[81]
10 wt% PtRu-$LiCoO_2$	25	2.1	n.i. [d]	560	[78]
10 wt% PtRu-$LiCoO_2$	25	1.1	100	53	[79]
10 wt% PtRu-Co_3O_4	25	1.1	100	85	[79]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

Table 5. Performances of the C supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
9 wt% Co-C	30	0.2	100	0.2	[30]
10 wt% Co-C	20	1.1	100	136	[84]
1 wt% Ru-C	40	0.1	n.i. [d]	0.7	[87]
2 wt% Ru-C	20	0.3	n.i. [d]	35	[33]
5 wt% Ru-C	25	0.2	n.i. [d]	13.6	[85]
10 wt% Ru- CF [e]	20	2.1	n.i. [d]	14.2	[76]
1 wt% Rh-C	40	0.1	n.i. [d]	1.1	[87]
1 wt% Pd-C	40	0.1	n.i. [d]	0.1	[87]
10 wt% Pd-C	23	< 0.1	100	< 0.1	[86]
1 wt% Pt-C	40	0.1	n.i. [d]	0.7	[87]
1 wt% Pt-C	20	0.4	98	2.9	[89]
2 wt% Pt-C	30	1.1	64	5.0	[84]
20 wt% Pt-C	20	2.1	100	115.0	[83]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

[e] CF : Carbon Fibers.

Table 6. Performances of the metal oxide supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
9 wt% Co-γAl_2O_3	30	0.2	100	1.0	[30]
9 wt% Co-γAl_2O_3	30	3.2	100	2.4	[30]
1 wt% Rh-γAl_2O_3	40	0.1	n.i. [d]	0.4	[87]
2 wt% Ru-γAl_2O_3	30	2.5	70 [e]	4.8	[92]
1 wt% Pt-γAl_2O_3	40	0.1	n.i. [d]	0.2	[87]
2 wt% Pt-γAl_2O_3	30	1.1	81	2.9	[90]
1 wt% Ru-TiO_2	20	0.4	n.i. [d]	15.6	[94]
1 wt% Ru-TiO_2	40	0.1	n.i. [d]	1.6	[87]
1 wt% Rh-TiO_2	40	0.1	n.i. [d]	3.0	[87]
1 wt% Pd-TiO_2	40	0.1	n.i. [d]	0.2	[87]
1 wt% Pt-TiO_2	40	0.1	n.i. [d]	1.4	[87]
1 wt% Pt-TiO_2	20	0.4	n.i. [d]	3.7	[94]
2 wt% Pt-TiO_2	20	0.4	n.i. [d]	4.8	[93]
2 wt% Pt-ZrO_2	20	0.4	n.i. [d]	2.1	[93]
1 wt% Ru-ZrO_2-SO_4^{2-}	20	0.4	98	10.5	[89]
1 wt% Pt-ZrO_2-SO_4^{2-}	20	0.4	n.i. [d]	0.3	[89]
2 wt% Pt-ZrO_2-SO_4^{2-}	20	0.4	n.i. [d]	2.4	[93]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

[e] The reaction was ceased when 70 % conversion was achieved [97].

Table 7. Performances of the supported alloys.

Supported alloys	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
1.4 wt% PtPd-CNT [e]	29	< 0.1	100	9.0	[91]
16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-CF [f]	20	2.1	n.i. [d]	41.7	[76]
13.3 wt% $Ru_{75}Co_{25}$-CF [f]	20	2.1	n.i. [d]	37.1	[76]
1 wt% RuCu-TiO_2	20	0.4	n.i. [d]	3.1	[94]
1 wt% RuPd-TiO_2	20	0.4	n.i. [d]	6.0	[94]
1 wt% Ru_2Pt_1-TiO_2	20	0.4	n.i. [d]	15.2	[94]
1 wt% RuPt-TiO_2	20	0.4	n.i. [d]	10.0	[94]
1 wt% Ru_1Pt_2-TiO_2	20	0.4	n.i. [d]	10.0	[94]
1 wt% RuAg-TiO_2	20	0.4	n.i. [d]	3.9	[94]
2 wt% PtPd-TiO_2	20	0.4	n.i. [d]	4.2	[93]
2 wt% PtIr-TiO_2	20	0.4	n.i. [d]	3.2	[93]
1 wt% PtAg-TiO_2	20	0.4	n.i. [d]	2.6	[94]
2 wt% PtAg-TiO_2	20	0.4	n.i. [d]	2.6	[93]
10 wt% PtRu-Co_3O_4	25	1.1	100	85.0	[79]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

[e] CNT: Carbon NanoTubes.

[f] CF : Carbon FIbers.

Table 8. Reachable power levels at about room temperature for the best catalysts given in Tables 1 to 7.

Catalyst	GHSC [a] wt%	Mass for 100 W [b] g	Power for 1 g(metal) [c] W	Reference
$CoCl_2$	6.8	0.088	1140	[38]
CoB	4.2	0.909	110	[53]
CoB-Ni	4.2	0.091	1100	[62]
CoWB-Ni	4.2	0.067	1500	[65]
CoP-Cu	2.1	1.000	100	[73]
Ru	4.2	0.250	400	[16]
$Ru_{60}Co_{40}$	2.1	0.057	1750	[76]
$Ru_{80}Fe_{20}$	2.1	0.055	1830	[76]
$Ru_{60}Co_{20}Fe_{20}$	2.1	0.037	2680	[76]
10 wt% Ru-$LiCoO_2$	2.1	0.002	42800	[78]
1.5 wt% Pt-$LiCoO_2$	4.2	0.005	20300	[27]
10 wt% Pt-$LiCoO_2$	2.1	0.003	30000	[78]
10 wt% PtRu-$LiCoO_2$	2.1	0.002	56000	[78]
10 wt% Ru-CF	2.1	0.070	1420	[76]
20 wt% Pt-C	2.1	0.009	11500	[83]
9 wt% Co-γAl_2O_3	3.2	0.417	240	[30]
2 wt% Ru-γAl_2O_3	2.5	0.021	4800	[92]
16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-CF	2.1	0.024	4170	[76]
13.3 wt% $Ru_{75}Co_{25}$-CF	2.1	0.027	3710	[76]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Mass of metal (active phase) for powering a 100 W fuel cell [16].

[c] Power level of a H_2-powered PEMFC when 1 g of metal (active phase) generates H_2 from $NaBH_4$.

Figure 1. Catalysed hydrolysis of sodium borohydride: a reaction full of issues.

Figure 2. Evolution of the gravimetric hydrogen storage capacity (G.H.S.C. in wt%) of the fuel [$NaBH_4$+(2+x)H_2O] with the excess of water (x).

Figure 3. Ideal gravimetric hydrogen storage capacity of the $NaBH_4$ storage solutions.

Sodium borohydride hydrolysis as hydrogen generator: issues, state of the art and applicability upstream from a fuel cell

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Abstract

Today there is a consensus regarding the potential of $NaBH_4$ as a good candidate for hydrogen storage and release via hydrolysis reaction, especially for mobile, portable and niche applications. However as gone through in the present paper two mains issues, which are the most investigated throughout the open literature, still avoid $NaBH_4$ to be competitive. The first one is water handling. The second one is the catalytic material used to accelerate the hydrolysis reaction. Both issues are object of great attentions as that can be noticed throughout the open literature. This review presents and discusses the various strategies which were considered until now by many studies to manage water and to improve catalysts performances (reactivity and durability). Published studies show real improvements and much more efforts might lead to significant overhangs. Nevertheless the results show that we are still far from envisaging short-term commercialization.

Keywords

Hydrogen; Hydrogen storage; Sodium borohydride; Sodium tetrahydroborate; Fuel cell.

1. Introduction

The unanimous opinion is hydrogen (H_2) has a great potential as energy carrier, particularly as a fuel for fuel cell applications. Nevertheless in order that a H_2 economy develops, some significant issues have to be addressed. One of the drawbacks with H_2, which is also one of its main challenges, is related to its storage. Indeed today several ways for storing H_2 e.g. high pressure, liquid hydrogen, metallic and chemical hydrides, and so on, are being investigated but none of them reaches yet satisfactory storage capacities from an application point of view. Among the various possibilities, chemical hydrides like e.g. sodium borohydride (sodium tetrahydroborate, $NaBH_4$) are viewed as having great potentials thanks to their high gravimetric/volumetric hydrogen storage capacities [1-3].

$NaBH_4$ (for its physical and chemical properties, see references [2,4-11]) is a well known chemical because it is often used in e.g. organic chemistry as reducing agent. $NaBH_4$ as a hydrogen storage material has a 60-year-old history, which has interestingly been reported briefly by Wee et al. [12,13] and at length by Demirci and Miele [14]. Discovered in the 1940s [15], its potential as hydrogen releasing material was remarked by the U.S. Army [10] and soon drew scientist's attention. However it was given up for a while from the middle of the 1960s. Recently, that is in the late 1990s, it met a new interest [16,17]. Amendola et al. [17] drew up a list of $NaBH_4$ advantages, amongst them we can cite e.g. non flammability of $NaBH_4$ solutions, stability in air for months, stability of reaction by-products which are environmentally safe and can be recycled. Though a prototype based on $NaBH_4$ hydrolysis has been constructed [16,17], H_2 generation through this reaction does not appear mature enough. Several issues like e.g. water handling, catalyst reactivity and deactivation, treatment of by-products and so on [12], hinder its development and do not permit to reach e.g. gravimetric hydrogen storage capacity (GHSC) that is satisfactory for an application point of view. Actually it is important to note here that the US Department of Energy has recommended no-go for the aqueous solution of sodium borohydride as a hydrogen storage solution for on-board vehicular hydrogen storage. We would like to emphasise that this recommendation has not envisaged storage for portable devices and storage ways alternative to the aqueous solution.

Hydrogen stored in $NaBH_4$ must be recovered either by thermolysis [14,18] or by hydrolysis [12]:

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

The latter reaction is much more investigated for several reasons, especially three. First, the hydrolysis of $NaBH_4$ is a spontaneous [19,20], exothermic reaction ($-210\ kJ\ mol^{-1}$ [21]) that besides can be accelerated thanks to a well chosen metal-based catalyst. Second, pure H_2 [21] can then even be produced at low temperatures (0-20 °C). Third, the fuel $NaBH_4$-H_2O stores 10.8 wt% of hydrogen and H_2O provides half of the H_2 [23]. However this reaction shows different hurdles. The first of them is both low solubility of $NaBH_4$ and solvation of sodium metaborate ($NaBO_2$) as by-product which implies that an important amount of water is needed to conduct the reaction. A second one is linked to the slow reaction rate. Indeed for practical reasons (e.g. storage) NaOH is added to the solution of $NaBH_4$ to slow down the self-hydrolysis which occurs when water is added to $NaBH_4$. Therefore an efficient catalyst is needed to decrease the activation energy and to accelerate the hydrogen generation rate (HGR). Both hurdles are the most studied ones as that can be remarked throughout the open literature.

In the next sections we propose to list and to discuss the strategies used to overcome these two main challenges. Note that there are other issues regarding the hydrolysis reaction: e.g. $NaBH_4$ production process which is expensive and $NaBO_2$ recycle [12,24,25]. More general reviews are available throughout the open literature. Wee et al. [12] discussed the latest research (till 2005) on the use of H_2 generated via $NaBH_4$ hydrolysis and listed the advantageous features of this reaction. More recently, Demirci [26] reported basics and advantages of $NaBH_4$ as hydrogen carrier. Çakanyıldırım and Gürü [25] reviewed the production of $NaBH_4$, more briefly its dehydrogenation and the $NaBO_2$ recycle. Anyway, some other issues are briefly tackled in the last section of the paper. To summary, the present review focuses the water handling challenge as well as the catalytic materials challenge because they are the most studied ones.

Prior to any discussion, it is very important to highlight a fundamental point. The storage capacity of $NaBH_4$ or system $NaBH_4$-H_2O is mostly discussed on the basis of the GHSC (wt%). However, there is a mistake that is often made throughout the open literature. The GHSC is generally calculated on the basis of only $NaBH_4$ and H_2O while this must be done on the basis of the complete storage system (including the tank, storage media, safety system, valves, regulators, piping, and so on). Indeed the GHSC is a system target. It is therefore to note that the following discussion tackles the GHSC as it is throughout the open literature (i.e. on the basis of $NaBH_4$-H_2O) while keeping in mind that they are overestimated.

2. Water handling challenge

From a theoretical point of view hydrolysis of 1 mole of $NaBH_4$ requires only two moles of H_2O:

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

but in real conditions the reaction needs more water to release 4 moles of hydrogen and can be written as :

$$NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O + 4\ H_2$$

with x the excess of water. Two reasons justify the utilization of an excess of water during $NaBH_4$ hydrolysis (Figure 1). The most important one is linked to $NaBH_4$ solubility in water. As reported by Kojima et al. [27], the $NaBH_4$ solubility at 25 °C is 55 g per 100 g water [28] or 1.46 mol per 5.56 mol. Accordingly the GHSC of such a fuel is 7.5 wt% (whereas 10.8 wt% with $x = 0$). However Kojima et al. [27] added that since the solubility of the by-product $NaBO_2$ is 28 g per 100 g water, the $NaBH_4$ concentration at 25 °C should be below 16 g per 100 g water to keep the liquid state of $NaBO_2$, which precipitation could cause losses in the catalytic performances. In that case the GHSC of the fuel is 2.9 wt%. This value is much lower than the claimed 10-20 wt% of most of the chemical hydrides [1].

The second reason justifying the excess of water is the fact that the stable form of the reaction by-product $NaBO_2$ is its hydrated form ($NaBO_2.xH_2O$) [25]. Figure 2 shows the evolution of the GHSC of the fuel $NaBH_4+(2+x)H_2O$ with the excess of water x. With $x > 3$, the GHSC is below 6 wt%, and this value is a criterion for 2010 settled by the U.S. Department of Energy (DOE) for automotive applications [29]. Beyond year 2015, it is expected capacities > 9 wt%, which excludes any excess of water ($x = 0$). Çakanyildirim and Gürü [25] has reported that a value of $x = 0.84$ should be enough to achieve a capacity of 9 wt%. However, as already noticed above, the values 6 and 9 wt% are system targets that includes all components of the complete storage system. Accordingly the system capacity of $NaBH_4$ is realistically < 3 wt% when $x > 3$ and 4.5 wt% when $x = 0.84$.

How reducing x, *i.e.* how optimising the GHSC of the fuel $NaBH_4+(2+x)H_2O$ is thus one of the main objectives of the different studies conducted. The next sections draw up and discuss the different alternatives which are studied to handle this problem.

2.1. Optimisation of the molar ratio $H_2O/NaBH_4$ of aqueous solutions

The first studies reporting hydrogen release capacities of $NaBH_4$ envisaged a hydrolysis reaction with a high $H_2O/NaBH_4$ molar ratio. For example, Schlesinger et al. [15] used an aqueous solution with a molar ratio $H_2O/NaBH_4$ of 42 (i.e. GHSC < 2 wt%). Among the most recent articles, Amendola et al.'s [16], reported a lower ratio but still higher than the ideal $x = 0$, that is a ratio of about 7 (i.e. GHSC = 4.2 wt%, stabiliser weight being taken into account). Xu et al. [30] suggested that in the viewpoint of practical application a $NaBH_4$ concentration of 15 wt% should be set in order to keep the by-product solution state and get relatively high hydrogen storage efficiency. However in such conditions the GHSC can only reach 3.2 wt%. Shang et al. [31] addressed the water excess issue through thermodynamic modelling. The optimal concentration of $NaBH_4$ was calculated while taking into account both possible precipitation of $NaBO_2$ and NaOH addition. It was showed that the maximum GHSC of the system $NaBH_4$-NaOH-H_2O is 2.2 wt% at 20 °C, which corresponds to a NaOH concentration of 0 wt%. The capacity decreases with increasing the NaOH concentration. At 80 °C, the maximum capacity is 5.1 wt% (with 0 wt% NaOH). On the other hand, Liu et al. [32] investigated thermal properties of $NaBH_4$-NaOH-H_2O. Firstly it was showed that it is possible to store and use the $NaBH_4$ solution below 0 °C if the NaOH concentration is less than 20 wt%. Secondarily the optimum composition for stabilising the $NaBH_4$ solution is 15 wt% $NaBH_4$ in 10 wt% NaOH considering both liquidus temperature and GHSC. This composition fits a GHSC of 3.2 wt%.

Another solution, maybe the most obvious, is to optimise the features of the hydrolysis reaction medium by decreasing the water content to a minimum. Hua et al. [33] showed that a GHSC of 6.7 wt% could be reached at room temperature with about 90 % of $NaBH_4$ conversion efficiency. In the experimental conditions 10 g of $NaBH_4$ was added to 18 g of H_2O, which is the solubility of $NaBH_4$ at 25 °C. It was noticed that considering the lower solubility of $NaBO_2$ and its stronger association with H_2O at lower temperature, small consumption of $NaBH_4$ should be expected. In addition, one may wonder about catalytic material durability because of possible $NaBO_2$ precipitation which can deactivate the catalyst. Such deterioration could lead to small conversion of $NaBH_4$ as well as lower HGR.

Although efforts were done to optimize the $H_2O/NaBH_4$ molar ratio the $NaBH_4$ solubility still prevents a satisfactory GHSC. This is one of the technical arguments that motivated the experts of DOE to recommend no-go for aqueous $NaBH_4$ solution [29]. Nevertheless, to by-pass the problem of $NaBH_4$ solubility, different studies envisaged to use $NaBH_4$ in a state which is different from aqueous solution. It is what we propose to describe below.

2.2. Utilization of $NaBH_4$ under various forms

2.2.1. Powder

The utilization of $NaBH_4$ powder is not a new idea. It was first introduced by Kong et al. [34] who studied H_2 generation from various hydrides. In that case water vapour is used instead of liquid water. The idea is basically to store solid $NaBH_4$ while H_2O vapour is recovered from a fuel cell. Accordingly the GHSC would be 21.3 wt% (the weight of H_2O vapour is not considered in the calculation because it is supposed to be generated in a fuel cell and so not stored anywhere). However Kong et al. [34] observed that $NaBH_4$ did not react with H_2O vapour. Despite this failure, the idea of using solid $NaBH_4$ was considered one more time. Marrero-Alfonso et al. [35,36] reported that the reaction of $NaBH_4$ with steam produced H_2 and a hydrated solid, and that up to 95% yield of H_2

was obtained with pure steam without any catalyst. Thermogravimetry and X-Ray Diffraction analysis revealed that the solid by-product was a hydrated borate corresponding to $NaBO_2.2H_2O$. The dihydrate form of $NaBO_2$ is the stable form at temperatures up to 105 °C and the degree of hydration of the product is not a direct function of water/hydride ratio originally present in the system [36]. According to Kong et al. [34], 21.3 wt% is the highest hydrogen density if only $NaBH_4$ is considered as being initially stored in the case of an on-board application (Figure 3). Can this ideal value be reached when $NaBO_2.2H_2O$ is the reaction product? In order to attempt to answer this question, let us consider an example. For an on-board application the weight of the stored contents in the tank is crucial (the volume is not regarded) and thus the hydrated by-product weight is the limiting factor. If the up-limit of the tank is 1000 g, this one will only store 1000 g of $NaBO_2.2H_2O$ or, initially, 371 g of $NaBH_4$ (supposing equivalent the densities of both reactant and by-product). Accordingly the effective $NaBH_4$ GHSC of the tank will only represent 37 % of its maximum capacity. Now if one supposes that 1000 g of $NaBH_4$ is equivalent to a GHSC of 21.3 wt%, 371 g of $NaBH_4$ will be equivalent to 7.9 wt%. Note that if the reaction by-product is anhydrous $NaBO_2$, the effective capacity will be equivalent to 12.2 wt%. This trivial calculation illustrates the issues due to the formation of stable hydrated by-products. Marrero-Alfonso et al. [36] wrote that the fact that $NaBO_2.2H_2O$ appears to be a favoured product will complicate the process design. We agree. Another example of complication which could be a limited or hindered diffusion of water vapour through a superficial layer of hydrated $NaBO_2$. This possible issue was also suggested by Çakanyıldırım and Gürü [25]. A solution can be a stirring system, which mixes the whole solid for dragging the reaction by-products far from the water inlet. However that may be, the idea of using H_2O vapour is good but this one has not been developed yet. With the deepening of the studies and with the benefit of hindsight, the system might be improved and optimised, knowing that every improvement should permit to reach effective GHSC above the specification 9 wt%, the ideal limit being none other than 21.3 wt%. Furthermore no catalyst has been added to solid $NaBH_4$ yet.

Another solution which could be envisaged is to use stoichiometric proportions of liquid water and solid $NaBH_4$. This is what Kojima et al. [37] applied. They observed that by increasing the pressure, the hydrogen yield is twice better. They introduced the catalyst (Pt-$LiCoO_2$) mixed with $NaBH_4$ in a closed pressure vessel and then a stoichiometric amount of H_2O was injected. The GHSC (including the catalyst) was 9.0 wt%. From our calculations based on the values given by Kojima et al. [37] (i.e. catalyst/$NaBH_4$ = 0.2 g/1 g), the maximum GHSC was 9.8 wt%. The GHSC that was reached by this process is outstanding because it is high enough to reach the DOE targets for automotive applications. However such hydrolysis system induces some questions, especially from practical point of view. Will all of the generable H_2 be produced in one time? Or will it be possible to use this system during transition stages (go-and-stop)? If generated H_2 is immediately consumed by a fuel cell the H_2 pressure could not increase anymore and in that case will the GHSC of 9.0 wt% be reached? What was the hydration degree of $NaBO_2$? Is there any dependence between $NaBO_2$ hydration degree and H_2 pressure? In fact, all of these questions can be grouped together in a single one: is 9.0 wt% reachable in fuel cell vehicle application? Recently, Liu et al. [38] published a work that is slightly different from Kojima et al.'s [37]. The main difference with Kojima study relies on non-pressurized system. Hydrogen could be liberated at very high rates ($CoCl_2$-catalysed), such as over than 90 % conversion rates were achieved. Final H_2 generation capacity was achieved as high as 6.7 wt%. This study is actually quite similar to Hua et al.'s [33] even if in their conception they are different since the former used the reactant in its solid form while the latter used an aqueous solution. In both studies, the molar ratio of H_2O to $NaBH_4$ was about 4 and the same GHSC were reached, i.e. 6.7 wt%. Accordingly, the advantage of using solid $NaBH_4$ is not so obvious. Water diffusion onto the catalytic surface for the solid system should be much more limited and difficult than for an aqueous solution. In fact, a comparative study of both configurations lacks. Cento et al. [39] also considered solid $NaBH_4$ but they mixed it together with the catalyst (salt of Ni or of Fe). Excess of water was then added to the mixture to start the hydrolysis reaction. Today the investigations are in their early stages but there is no doubt that new results and findings will be soon published.

2.2.2. *Gel*

Recently, Liu et al. [40] reported an original, innovative solution. A sodium polyacrylate was used as super absorbent polymer (it can absorb water, as much as 200–800 times its own mass) to form alkaline $NaBH_4$ gel and explored its possibilities for $NaBH_4$ hydrolysis. It was found that the absorption capacity of sodium polyacrylate decreased with increasing $NaBH_4$ concentration. For example, for a stabilised (5 wt% NaOH) solution at 25 wt% of $NaBH_4$ the polymer was able to adsorb at about 5 times in weight, what corresponds to a GHSC of 4.5 wt% (but the amount of catalyst is not taken into account). H_2 generation from the gel was carried out using $CoCl_2$ catalyst precursor solutions. It was higher than that obtained from an alkaline solution. Typical experimental conditions were 30 g of gel and 15.2 g of $CoCl_2$ solution, what implies a GHSC of about 3 wt%. The idea of using an adsorbent is good but the preliminary results must be developed in order to reach higher GHSCs. Optimisations (e.g. modified polymer, optimised solution, addition of additive, and so on) may again improve the capacities. Furthermore, using such storage system can solve application issues. For example, Liu et al. [45] reported that with the $NaBH_4$ gel power generation devices can be placed in all directions without preference and can avoid impurities like $NaBH_4$, $NaBO_2$ and NaOH. It was besides reported that borohydride ions diffuse in alkaline gel particles quicker than in alkaline solution. Furthermore, in our opinion the polymer could be a potential support for a metal catalyst like e.g. cobalt or cobalt boride, the polymer having then a double role, which is to store both $NaBH_4$ and H_2O and to support the catalytic material. Nevertheless questions arise. Is the polymer stable enough to suffer the alkalinity of the borohydride solution as well as the presence of catalyst? What is the gel behaviour when $NaBO_2$ precipitates since it solubility is well below that of $NaBH_4$?

To conclude, it can be remarked that the highest GHSC (Figure 3) that might be reached by using $NaBH_4$ gel is 7.5 wt% (for 55 g of $NaBH_4$ per 100 g of H_2O, the solubility of $NaBO_2$ and the amount of NaOH being not taken into account). For some portable applications, this storage system could be the ideal solution. The idea of using a matrix (e.g. polymer) for storing $NaBH_4$ and/or H_2O and/or catalyst must be further developed.

2.2.3. *Methanolysis as an alternative of hydrolysis?*

There are generally two ways to face an issue. The first one is to try to optimize of the experimental conditions as reported in the previous sub-sections. The second way is simply to by-pass the problem by changing the experimental approach. The latter way is what Lo et al. [41] chose to do. To avoid the formation of the hydrated reaction product, an alternative to H_2O utilization as reactant is the use of a primary alcohol. Indeed $NaBH_4$ is known to be reactive to e.g. methanol and ethanol [42] and methanol has the highest reactivity toward $NaBH_4$ [41]. The overall reaction between methanol and $NaBH_4$ can be described as:

$$NaBH_4 + 4\ CH_3OH \rightarrow NaB(OCH_3)_4 + 4\ H_2$$

This system has a 4.9 wt% GHSC (Figure 3). Lo et al. [41] assessed the H_2 generation in methanol and mixtures of methanol and water ($H_2O/NaBH_4$ mole ratio of either 2 or 10). The best system was the mixture with a mole ratio of 10. However Lo et al. [41] recognised that methanolysis of $NaBH_4$ will not likely meet the DOE criterion of 9.0 wt% hydrogen storage system density for automotive fuel cells by 2015 as it is also the case for the base-stabilised hydrolysis. This is all the more true because the maximum GHSC is 4.9 wt%. It is thus impossible to increase this value.

Due to a maximum GHSC below 5 wt%, one can rightfully wonder about the interest of such a system based on the utilisation of methanol. What could be the advantage(s) of using methanol instead of water? Is it relevant to consider methanol as a potential fuel while it is known as being toxic (instead of safe water)? Is the methanolysis reaction product $NaB(OCH_3)_4$ recyclable? Or is it more easily recyclable than $NaBO_2$? If the methanolysis is metal-catalysed, should one expect the generation of secondary by-products like e.g. carbon monoxide and carbon dioxide? All of these questions perplex. Even the utilisation of methanol vapour will not improve the GHSC of 4.9 wt%.

The investigations about the system $NaBH_4$-CH_3OH are in their early stages. The utilisation of methanol may be viewed as a potential solution in order to avoid the problems due to the formation of hydrated by-products.

2.3. Summary

A GHSC of 10.8 wt% is attractive. $NaBH_4$ has this property but the effective capacities are unfortunately well below this ideal value for two main reasons: the use of water excess to lead $NaBH_4$ solubility and the hydration of the reaction by-product $NaBO_2$. Typically the first studies reported capacities < 2 wt%. To overcome the water excess issue, several solutions were proposed. These solutions permitted to improve the effective GHSCs. For example, with highly concentrated aqueous solutions capacities of about 7 wt% were obtained while with solid $NaBH_4$ capacities up to 9.0 wt% were observed. The thermodynamically stable form of

$NaBO_2$ is the dihydrated one [35,40], which means a maximum GHSC of 7.3 wt%. For obtaining higher capacities, the $NaBO_2$ hydration issue should be addressed.

In less than 10 years the effective GHSCs have improved reaching values closer to the ideal capacity. Even if for some of the proposed solutions the maximum own effective GHSC appears to be reached, for others and especially for the storage of solid $NaBH_4$, H_2O being provided as vapour, capacities up to 21 wt% could ideally be obtained.

However, it is here important to note one more time that the discussed GHSCs are only based on $NaBH_4$ and H_2O. If one now considers the complete storage system, it is evident that the values that have been experimentally evidenced fall short of the targets set for automotive applications. For example, if one arbitrarily supposes that the components of a storage system weigh 50% of the total weight, the GHSCs listed above should be divided by a factor of 2. And, the highest GHSC that might be expected is 10.8/2, namely 5.4 wt%. Such value confirms that $NaBH_4$ cannot be considered for automobile applications but it still has a potential for mobile, portable and niche applications.

Throughout the present section as well as in the papers cited here, the volumetric hydrogen storage capacity (VHSC) has never been tackled. It is generally not taken into account because of two main reasons. First, the hydrolysis is in most cases performed in diluted solution, which strongly penalizes the VHSC. Second, since the GHSC falls short of the application targets, the VHSC is even not considered. However that may be, the VHSC is as important as the GHSC.

Stored hydrogen has to be generated for fuelling fuel cell. The HGR is then a critical parameter since it will depend on the power of the fuel cell. This means that the production should be efficient enough to permit variable HGRs and maximum yields. This is the role of the catalyst.

3. Catalytic materials challenge

H_2 can be released spontaneously by self-hydrolysis [19,20,43]. It was reported that the rate at which $NaBH_4$ self-hydrolyses in water (without catalyst) depends on the pH and solution temperature [19]. The rate is empirically represented by

$$\log(t_{1/2}) = pH - (0.034T - 1.92)$$

with $t_{1/2}$ the time (min) it takes for one-half of a $NaBH_4$ mole to decompose versus temperature (K) [44]. To avoid the self-hydrolysis, due to the fact that such spontaneous reaction is undesirable from an application point of view, $NaBH_4$ aqueous solution is stabilised by making it alkaline through addition of sodium hydroxide (or eventually potassium hydroxide) [19]. For example, for pH 14 and at 25 °C (298 K), $NaBH_4$ solutions have a half-life time of 430 days [17]. Therefore catalysts must be used to accelerate H_2 generation by $NaBH_4$ hydrolysis. According to Wee et al. [12] the most important factor involved in the successful use of H_2 generated via $NaBH_4$ hydrolysis reaction is the preparation and development of optimum catalyst. As reported in this review catalysts used are exclusively transitions metal-based and are used in various forms: salt, bulk, nanoparticles, supported, and alloy (supported or not) [12].

The present section draws up the nature of these catalytic accelerators and discusses both their performances and their durability.

3.1. Catalysts nature

3.1.1. Acids

Utilization of acids to generate H_2 from $NaBH_4$ was studied mainly in the 1950-1960s. First, Schlesinger et al. [15] observed that the hydrolysis reaction was greatly accelerated by addition of acidic substances. In their study a large number of acids were tested like e.g. oxalic acid, citric acid or boric oxide. Then several papers reported fundamental studies determining e.g. the kinetics and the reaction mechanisms of the acid-catalysed hydrolysis of $NaBH_4$ [45-49]. Today acids are not investigated anymore. It appears that they are not regarded as potential accelerators and in our opinion it is regrettable. For example, when solid $NaBH_4$ is stored, H_2O is supposed to be provided to start the H_2 generation. An acid solution might be as efficient as either a metal salt solution or a supported metal. Furthermore issues related to safety, catalyst recovery and recycling, cartridge/tank design might be (partially) solved. Acids have thus a potential.

3.1.2. *Metallic salts*

Today catalysts used are metal-based materials. The first metal-based materials used are metal salts (Table 1) [15,38,50,51]. Schlesinger et al. [15] had tested manganese, iron, cobalt, nickel and copper chlorides. They reported that particularly striking was the catalytic effect of certain metal salts, especially that of cobalt chloride. The kinetics of cobalt chloride-catalysed hydrolysis was studied and a first-order reaction with respect to the $NaBH_4$ concentration and activation energies of 17.5 to 29.5 kcal mol^{-1} depending on the sodium borohydride concentration were reported [52]. Later Brown and Brown [50] screened much more metal salts (Table 1), especially noble metal-based salts. Platinum was a highly effective catalyst, more effective than cobalt. Both ruthenium and rhodium were more active catalysts but palladium exhibited much poorer catalytic activity. Kaufman and Sen [49] investigated various salts based on the same metals than those studied by Schlesinger et al. [15]. It was especially found that the catalytic activity of the metal salts was dependent on the cation (Co^{2+}, Cu^{2+} and Ni^{2+}) while it was independent of the anion (Cl^-, NO_3^- and $CH_3CO_2^-$). Recently Liu et al. [51] compared cobalt chloride, nickel chloride and for the first time nickel fluoride. The highest reactivity of the cobalt salt was confirmed but the HGR was much lower than the rates obtained in references [15,50]. This may be explained by the fact that Liu et al. [51] stabilised the aqueous solution with 10 wt% NaOH. The nickel fluoride was 3 times more reactive than the nickel chloride but it was much less reactive than cobalt chloride this does not make it a suitable catalytic material. Liu et al. [38] reported HGRs of about 11 $L(H_2)$ min^{-1} $g^{-1}(Co)$ for cobalt chloride and gravimetric hydrogen storages up to 6 to 7 wt% ($NaBH_4$ was stored as solid and aqueous solution cobalt chloride was added). To our knowledge, this performance is likely the best ever reported for the cobalt chloride salt.

Table 1 list the performances of the metal salts tested. Obviously the noble metal-based salts are the most reactive ($RuCl_3$, $RhCl_3$ > H_2PtCl_6). They are followed by cobalt chloride, which appears to be a promising alternative to noble metals because it is reactive while being cheaper. This explains why most of the published papers deal with the improvement of the cobalt-based catalysts reactivity (see the next sub-sections). However Schlesinger et al. [15] reported that the effect of the cobalt salt is ascribed to the catalytic action of cobalt boride Co_2B, which is formed in the initial stages of the reaction. Typically it was observed that the salts reacted rapidly with $NaBH_4$ solutions and gave finely-divided black precipitates [15,50]. According to Schlesinger et al. [15] the precipitates were probably borides. According to Brown and Brown [50], the precipitates were the noble metals (e.g. platinum) reduced to the elementary state. In both cases, it was remarked that the precipitates were active, effective catalysts for the hydrolysis of $NaBH_4$. Therefore Schlesinger et al. [15] and Brown and Brown [50] considered that the active catalysts were cobalt boride and platinum (0), respectively. Accordingly metal borides like e.g. cobalt or nickel borides are today much investigated (discussed in the next sub-section).

3.1.3. *Metal borides*

Cobalt boride has drawn a particular attention to itself. Jeong et al. [53], Wu et al. [54] and Walter et al. [55] prepared cobalt boride by the chemical reduction method using $NaBH_4$ as a reduction chemical. This method is in fact the most common for obtaining metal borides. In addition, Wu et al. [54] heat-treated the obtained CoB at various temperatures. It was observed that the catalyst treated at 500 °C exhibited the best catalytic activity because it had the best crystallisation (the more crystallised, the more active). This material achieved an average HGR of about 3 $L(H_2)$ min^{-1} $g^{-1}(CoB)$. According to Wu et al. [54], this rate may give a successive H_2 supply for a 481 W PEMFC at 100 % H_2 utilisation. Liu et al. [51] compared the catalytic activity of Co_2B to that of cobalt powder, cobalt chloride and Raney cobalt. Co_2B (468 $mL(H_2)$ min^{-1} g^{-1} (Co_2B)) was better than the powder (126 $mL(H_2)$ min^{-1} $g^{-1}(Co)$) and the Raney (268 $mL(H_2)$ min^{-1} g^{-1} (Co)) but was less active than the chloride (570 $mL(H_2)$ min^{-1} $g^{-1}(Co_2B)$). Patel et al. [56,57] used CoB-based thin film catalyst synthesised by pulsed laser deposition technique which permitted the formation of CoB nanoparticles. It was observed that cobalt was efficient only when alloyed with boron which partially prevents metal oxidation.

Modified CoB-based catalysts were besides investigated. Ingersoll et al. [58] reported nickel-cobalt-boride NiCoB (molar ration Ni:Co of 1:1) that were prepared by the chemical reduction method. Nickel is also a metal which boride-based compounds were also studied. For example, Walter et al. [55] observed a maximum HGR of 1.3 $L(H_2)$ min^{-1} $g^{-1}(Ni_3B)$ for a Ni_3B catalyst. Hua et al. [33] claimed the preparation of a highly stable and active nickel boride catalyst (Ni_xB) even if its performance were four times lower than that of a Ru-based catalyst at room temperature. Ni_2B was tested by Liu et al. [51] but this catalyst was quite inefficient. Chen and Kim [59] synthesised nickel-boride-silica nanocomposites, the boride function being formed by the chemical reduction method using $NaBH_4$. At 25 °C, $NiB\text{-}SiO_2$ was three times less efficient than $Pt\text{-}SiO_2$.

A catalyst in powder form is not conceivable from an application point a view and that's why CoB was supported over a substrate, mainly nickel foam. Even if it is used as a substrate, catalyst-free Ni foam catalyses the hydrolysis of $NaBH_4$ [60]. Mitov et al. [61] electrodeposited CoB with Mn on nickel foam leading to CoMnB-Ni. Dai et al. [62] optimised an electroless plating method for the preparation of amorphous CoB catalyst supported on nickel foam (porous structure, low density, high thermal and chemical stability under the hydrolysis conditions). One of the highest HGRs was observed, i.e. 11 $L(H_2)\ min^{-1}\ g^{-1}$(CoB-Ni). In a further study, Dai et al. [62] modified the CoB-Ni catalyst by introducing a new element, that is, tungsten. The same electroless plating method was used. Via optimizing these preparation and reaction conditions, the CoWB-Ni material (87.0 wt% Co, 4.5 wt% W, 8.5 wt% B) achieved a HGR of 15 $L(H_2)\ min^{-1}\ g^{-1}$(CoWB-Ni). According to the authors, this rate is comparable to the highest level of noble metal catalyst. A CoB-Ni catalyst obtained by an electroless method was also reported by Krishnan et al. [63] but the performances were much less sharp. Liang et al. [64] suggested a new approach for optimising the catalytic ability of the catalyst: the modification of the nickel foam substrate. Cobalt boride supported over palladium modified nickel foam was prepared. It showed an average HGR of about 2.9 $L(H_2)\ min^{-1}\ g^{-1}$(CoB-PdNi). It was concluded that the presence of Pd has three advantages: it improves the catalysts stability; it increases the activity for H_2 generation because of its activity towards $NaBH_4$; and, it adsorbs and stores hydrogen during the process of H_2 generation.

Table 2 summarises the HGRs of the various metal borides discussed in the present section. It stands out that the most efficient material is CoWB-Ni [65] since it shows the best HGR (15 $L(H_2)\ min^{-1}\ g^{-1}$), the highest GHSC (4.2 wt%) and a maximum H_2 generation yield (100 %). This promising result shows that further improvements can be expected if the catalytic material, the hydrolysis medium and the hydrolysis conditions are further optimised. The great interest is that these materials must replace noble metals like e.g. Pt and Ru.

3.1.4. Reduced transition metals

Ruthenium is known to be the most reactive metal for hydrolysing $NaBH_4$. It has been used as catalytic accelerator of the prototype produced by Millenium Cell [16,17]. In that case, ruthenium as $RuCl_3$ was dispersed on an anionic exchange resin (acting as a substrate of the catalytic phase) and then reduced by addition of a solution of $NaBH_4$. However it is not clear whether the catalyst is either metallic Ru or ruthenium boride (Ru_2B). So in the present review paper it is supposed that ruthenium could be metallic. Walter et al. [55] also used ruthenium, the catalysts being obtained through the metal salt reduction. Özkar et al. [66,67] reported the use of ruthenium nanoclusters obtained from the reduction of $RuCl_3$ by $NaBH_4$ and stabilised by specific ligand (acetate ion). Recently Özkar et al. [68] employed ruthenium acetylacetonate but as homogeneous catalyst. After reaction this material was not reduced by $NaBH_4$ and remained unchanged.

Ruthenium is the most reactive metal but it is also the most expensive one. Hence it is essential to propose an alternate, cheaper, reactive metal. Liu et al. [51] tested cobalt and nickel in various states: fine metal powder, metal salt (see section 4.1.2), metal boride (see section 4.1.3) and Raney metal. In most cases cobalt showed higher catalytic activity than nickel but Raney Ni was as efficient as Raney Co. The tested Raney materials i.e. Ni, Co, $Ni_{25}Co_{75}$, $Ni_{50}Co_{50}$, $Ni_{75}Co_{25}$ were the most reactive ones. From density functional theory-based calculations, it is expected that Ni segregates at the surface when it is alloyed to Co and that the Co sites bind more strongly adsorbates [69]. Co should then be much more dispersed at the surface, what means much more Co active sites are available. This might be an explanation of the better reactivity of the Raney NiCo. Kim et al. [22,69] investigated filamentary nickel but the HGRs were of about 0.1 $L(H_2)\ min^{-1}\ g^{-1}$(Ni). Besides ruthenium, Özkar et al. [71] studied water-dispersible stabilized nickel nanoclusters, which according to the authors was a highly active catalyst even at room temperature.

Cobalt is maybe the most promising non-noble metal. With the objective to improve its reactivity, some studies worked on its modification. For instance Liu et al. [72] tried to fluorinate various metals (e.g. Ti, Mn, Fe, Co, Ni, Cu, Zn, Ru) in order to prevent the formation of oxide at the metal surface. Co-F showed the best performances but one can regret that no result for non-fluorinated Co is available to evaluate the real reactivity of CoF. Cho and Kwon [73] prepared Co-P catalysts electroplated on Cu (the pure Cu substrate was quite inactive towards $NaBH_4$ hydrolysis). It was observed that CoP-Cu (13 at% P) exhibited a catalytic activity 18 times higher than that of Co-P prepared in similar conditions. In a further study Cho et al. [74] prepared CoP-Cu by an electroless method and the optimised catalyst exhibited a HGR of 3.3 L(H_2) min^{-1} g^{-1}(CoP) at 30 °C, which was 60 times faster than that obtained with Co-Cu. Another way for improving the reactivity of Co was proposed by Malvadkar et al. [75] who prepared a nanoporous Co film by an oblique angle polymerization method using the nanostructured PPX-Cl film as a substrate. This material showed a promising performance with a HGR of 4.3 L(H_2) min^{-1} g^{-1}(Co) at room temperature.

Park et al. [76] investigated bimetallic and trimetallic alloys. Ru was chosen as a primary metal and e.g. Co, Ni, Fe, Ag, and Cu were chosen as secondary metals. HGRs of about 18.0 L(H_2) min^{-1} g^{-1}(metals) were observed for $Ru_{60}Co_{40}$ and $Ru_{80}Fe_{20}$ while the rate reported for Ru was of about 7.0 L(H_2) min^{-1} g^{-1}(Ru). The most efficient catalyst was $Ru_{60}Co_{20}Fe_{20}$ with a performance of 26.8 L(H_2) min^{-1} g^{-1}(metals).

The HGRs reported for the metals discussed above are summarised in Table 3. Compared to the metal salts (Table 1) and to some cobalt boride-based catalysts (Table 2), the metals do not show satisfactory performances. The highest rates are of about 27 L(H_2) min^{-1} g^{-1}(Ru,Co,Fe) [76] in a reaction medium storing 2.1 wt% of hydrogen. Actually besides the Park et al.'s work [76] the most promising study is Amendola et al.'s [16] since besides a HGR of 22 L(H_2) min^{-1} g^{-1} (Ru) obtained at 55 °C the GHSC was 4.2 wt%. Note that for most of the other metal catalysts, the GHSC was well below 1 wt%, often 0.1-0.2 wt%, and such values reveal experimental conditions that were rather favourable for reaching good catalytic reactivities. Reduced metal materials do not appear as being potential catalysts for accelerating the H_2 generation. Accordingly supported metals have been investigated in order that the support improves the metal reactivity.

3.1.5. Supported metals

Supporting an active phase like a transition metal is generally a good way for reducing the amount of metal while maintaining or even improving its reactivity. A support may have a geometric effect (e.g. dispersion of the metal) and/or an electronic effect (change in the electronic environment of the metal), what ideally improve the metals reactivity and/or durability.

Regarding the hydrolysis of $NaBH_4$, Kojima et al. [27] reported the first study dealing with supported transition metals. Various oxides as support (Co_3O_4, TiO_2, SiO_2, NiO, $LiMn_2O_4$, TiO, CoO, Ti_2O_3, $LiNiO_3$, $LiCoO_2$) and supported Fe, Ni, Pd, Ru, Rh and Pt catalysts were first screened. The 1.5 wt% Pt-$LiCoO_2$ catalyst showed the best performances. A HGR higher than 200 L(H_2) min^{-1} g^{-1} (Pt) was observed and it was stressed that this rate was 10 times faster than the Ru catalyst reported by Amendola et al. [16]. It was suggested that the lithium cobaltite ($LiCoO_2$) support adsorbs water that provides protons reacting with the hydrides of the borohydrides adsorbed over the Pt sites. In a further article, Kojima et al. [77] discussed the performance of testing of a hydrogen generator (gravimetric and volumetric hydrogen storage densities of 2 wt% and 1.5 kg H_2/100 L of $NaBH_4$ solution, respectively) using the Pt-$LiCoO_2$ catalyst that was coated over a honeycomb monolith. It was emphasised that for this storage system the volumetric density was similar to that of the compressed hydrogen at 25 MPa. From that moment, several research groups envisaged the utilisation of $LiCoO_2$. Krishnan et al. [78] alloyed Pt to Ru and compared 10 wt% PtRu-$LiCoO_2$ to both 10 wt% Ru-$LiCoO_2$ and 10 wt% Pt-$LiCoO_2$. The efficiency of PtRu-$LiCoO_2$ was almost double of that of the Ru- and Pt-based catalysts. Few years later, Krishnan et al. [79] tested various supports for dispersing PtRu: e.g. Co_3O_4, NiO, $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, TiO_2, ZrO_2. The best catalytic systems were PtRu-Co_3O_4 followed by PtRu-$LiCoO_2$. The superior reactivity of these supports was attributed to the formation of CoB in the presence of $NaBH_4$. Furthermore it was suggested that the formation of catalytically active CoB from $LiCoO_2$ was slower than that from Co_3O_4, what explained the highest performance of the latter support. The formation of cobalt boride from $LiCoO_2$ and Co_3O_4 was also noted by Simagina et al. [80], who reported a HGR of 4.0 L(H_2) min^{-1} g^{-1}($LiCoO_2$) for the former support at 40 °C (without any metal as active phase). In fact after these promising performances, $LiCoO_2$ was often used as support [80-83]. Table 4 shows the HGRs of the $LiCoO_2$-based supported metals.

Otherwise many other supports were used for dispersing e.g. Co, Ru, Rh, Pd or Pt: C [30,33,76,83-90], C nanotubes [91], γAl_2O_3 [30,84,87,88,92], SiO_2 [27], TiO [27], TiO_2 [27,87,88,93,94], Ti_2O_3 [27], $LiMn_2O_4$ [27], CoO [27], NiO [27], $LiNiO_3$ [27], ZrO_2 [93], ZrO_2-SO_4^{2-} [89,95].

Table 5 and Table 6 report the best performances of C- and metal oxide-based (mainly γ-Al_2O_3 and TiO_2) catalysts, respectively. Globally the papers cited here screened various supports without attempting to deeply explain the positive or negative bringing of the supports. For example, Wu et al. [83] compared three C supports with different specific surface areas (i.e. 170, 823 and 1196 m^2 g^{-1}) and observed that the specific surface area was not the crucial factor. However no hypothesis was suggested. It seems that in this case the geometric effects of the supports on the metal are negligible and the reactivity might be explained by likely electronic effects. Furthermore it would have been interesting to have information about the acidity of the supports. The C support has often competed with γAl_2O_3. Xu et al. [84] suggested that the higher catalytic activity of Pt-C in relation to that of Pt-γAl_2O_3 was due to the large specific surface area of the latter support (i.e. 1055 vs. 248 m^2 g^{-1}). Such observation was also reported by Simagina et al. [87] since it was showed that whatever the metal the activity of Pt, Rh, Ru, and Pd metals supported onto C (530 m^2 g^{-1}), γAl_2O_3 (170 m^2 g^{-1}) and TiO_2 (243 m^2 g^{-1}) decreased in the order $TiO_2 > C > \gamma Al_2O_3$. This ranking was then confirmed for Rh supported catalysts [88]. It was suggested that electronic effects could explain this ranking and that the rhodium chloride interaction with TiO_2 determined the reactivity of rhodium particles formed under action of $NaBH_4$ medium. On the other hand, whatever the support, the activity of these catalysts decreased in the order Rh > Pt = Ru >> Pd [87]. On the opposite, Xu et al. [30] found that Co-γAl_2O_3 was more effective than Co-C. Data about e.g. the acidity of the support, the redox properties of the catalyst (both metal and support), and the electronic structure of the metal could have been useful in order to attempt to explain such variations. Even if one has to recognise that the investigations are in an exploratory stage, one may regret that much more fundamental analyses were not performed.

Another way for improving the catalytic performances of a supported catalyst is to alloy the active metal with another one. For example, as already discussed above in this section Krishnan et al. [78] found that alloying Pt to Ru (with $LiCoO_2$ as support) led to a more efficient catalyst than Pt- or Ru-$LiCoO_2$. When alloyed to Pt, Ru should strongly antisegregate, what means that much more small Ru sites should be dispersed on the surface [69]. Moreover Ru should bind more strongly the adsorbate, i.e. borohydride, what could activate more easily the H_2 generation [69]. In other words, an electronic effect as well as a geometric effect could improve the reactivity. The Hammer and Nørskov's [69] density functional theory-based predictions give a possible explanation of the enhanced reactivity of the PtRu alloy with respect to the single metals. The PtRu alloying was also assessed for the support Co_3O_4 [79]. Demirci and Garin [93,94] also adopted such a strategy in order to improve the efficiency of their Pt-TiO_2 and Ru-TiO_2 catalysts, respectively. In fact Demirci and Garin [93,94] used density functional theory-based results available in references [69,96] in order to establish a list of alloys to be tested. RuCu, RuPd, RuAg and RuPt, all supported over TiO_2, were selected. For these alloys, it was expected that the Ru particles, which aggregate at the surface, are smaller and better dispersed than for a surface of pure Ru [69,94]. Furthermore the adsorption on the Ru sites of the alloys was expected to be higher [69]. However in both studies [93,94] the addition of a second metal to either Pt or Ru was either detrimental or inefficient. For example, Ru was alloyed to Cu, Pd, Ag and Pt (atomic ratio 1:1 or for RuPt atomic ratios x:y of 2:1 or 1:2) and the activity decreased in the order Ru, Ru_2Pt_1 > RuPt, Ru_1Pt_2 > RuPd > RuAg, Pt > RuCu > PtAg [94]. Demirci and Garin [94] regretted therefore that the theoretical predictions from references [69,94] were unfortunately not confirmed in their experimental conditions. Park et al. [76] adopted a much larger strategy. A high throughput screening test was set in order to compare a number of metal alloy compositions. Since efficient unsupported alloys were obtained (as discussed in the section 4.1.4), Park et al. [76] supported some of the most efficient alloys over carbon fiber. While the HGR of unsupported $Ru_{60}Co_{20}Fe_{20}$ was 26.8 L(H_2) min^{-1} g^{-1}(Ru,Co,Fe), that of 16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-C was 41.7 L(H_2) min^{-1} g^{-1}(Ru,Co,Fe). This result showed the important role of the support in the reduction process leading to dispersed, small metal particles. Finally, carbon nanotubes supported PtPd catalyst was suggested by Peña-Alonso [91] but according to the authors the Pt and Pd atoms were apparently dispersed elementally. Table 7 proposes a list of the best rates ever reported for supported alloys.

Globally the HGRs reported in Tables 5, 6 and 7 were obtained in mild experimental conditions. Furthermore most of the catalysts reached rates well below 10 L(H_2) min^{-1} g^{-1}(metal). Compared to the $LiCoO_2$-based catalysts (Table 3), the C, γAl_2O_3, TiO_2 or ZrO_2 supported catalysts are much less reactive.

3.2. Catalysts performances

3.2.1. Hydrogen generation rates

Tables 1 to 7 report the performances of the catalysts discussed in the previous section. The list is certainly not exhaustive but the best performances ever reported throughout the literature are all listed. The best catalysts can be ranked thanks to the value of the HGRs that are given. However these values do not give an idea of the power levels that could be generated. Amendola et al. [16] suggested a trivial calculation for estimating achievable power levels from their hydrogen generator. It was assumed a standard PEMFC operating at 0.7 V. In that case, generating 1 g(H_2) min^{-1} should be equivalent to 1125 W (i.e. 26.8 A h × 60 min h^{-1} × 0.7 V × 1 min^{-1}). That is, 1 L(H_2) min^{-1} should power a 100 W fuel cell. This calculation can be used as a reference for estimating the power levels reachable for the best catalysts. Dai et al. [65] used this calculation and asserted that assuming a 100 % yield, a hydrogen generation system using 10 g CoWB supported on Ni foam could power a 15 kW PEMFC.

Table 8 reports the power levels reachable with 18 of the most reactive catalysts at temperatures from 20 to 30 °C. The best catalysts are defined as being the materials generating more than 1 L(H_2) min^{-1} g^{-1}(metal) from a system $NaBH_4$-NaOH-H_2O storing more than 2 wt% hydrogen. From Table 8, the main observation is that with 1 g of active metal powers from 100 W to 56 kW can be reached. These power levels are rather sufficient for powering mobile, portable applications (1 W to few kW) as well as bikes (250-500 W), scooters (500 W to few kW) and small cars (50-100 kW). Obviously with more catalyst higher power levels could be proportionally obtained. For example, 1 g or 10 g of CoWB supported on Ni foam can power a 1.5 or 15 kW PEMFC, what matches the Dai et al.'s [65] calculations. However for all of the catalysts reported in Table 8, the GHSCs fall short of e.g. the specifications for cars (i.e. 6 wt% for year 2010 and 9 wt% for 2015).

A second observation from Table 8 is that with the highly active catalysts like e.g. 10 wt% PtRu-$LiCoO_2$ only 2 mg of noble metals (or 20 mg of the catalyst) is sufficient for generating 100 W. This is a great, promising progress in reducing the cost of the catalyst. Less the noble metal amount is, cheaper the catalyst is.

From the performance point of view, there are obviously promising catalytic systems. However a highly efficient catalyst is otherwise a durable catalyst.

3.2.2. Long-life tests

Given the large number of studies published since the late 1990s, one has no choice but to admit that the efforts devoted to the catalysts have not really focused on the durability while the catalyst performance was the primary objective. The durability studies are actually quite new.

Kim et al. [70] tested the durability of a filamentary Ni catalyst over 200 cycles. It was observed that 76 % of the initial H_2 generation remained at 200 cycles. The main interest of this study is that the catalyst surface was analysed prior and after the cycling tests. Interestingly it was observed that the catalyst agglomerated, what brought about the diminishing of the catalyst specific surface area with cycling and so to the reduction of reactive sites. Furthermore it was observed that with cycling a film spreading the catalyst surface was formed. The deactivating film consisted of $Na_2B_4O_7.10H_2O$, potassium borate (KB_xO_y) and boron oxide (B_2O_3). It was thus concluded that the catalyst deactivation resulted was due to both agglomeration and film formed. Note that this study is certainly the most complete since at our knowledge none of the other papers dealing with durability reported such observations.

Özkar et al. [67,68,71] applied a procedure similar to that applied by Kim et al. [70] for testing the durability of their catalysts. At 25 °C and for a borohydride solution storing about 0.1 wt% hydrogen, Ru [67], Ni [71] and Ni [68] nanoclusters provided 5170, 1450 (over 240 min) and 1200 (over 180 min) total turnovers in the hydrolysis of $NaBH_4$ before deactivation, respectively. Chen and Kim [59], Dai et al. [65], Xu et al. [84], and Demirci and Garin [93,94] applied 3 to 6 cycles only for testing the durability of their respective catalysts. In each case, the catalyst showed a good durability. Whatever the experimental conditions in each study, it is obvious that the durability tests were too superficial. Aware of that, Xu et al. [84] emphasised that the stability of their Pt-C catalyst during long operating period for successive H_2 generation needs to be studied. One can agree while regretting the lack of such studies. Nevertheless in another paper Xu et al. [30] investigated the durability of Co-γAl_2O_3 in continuous flow conditions (1 mL min^{-1} of a 5 wt% $NaBH_4$ solution). Even if the GHSC of the fuel was only of 1.1 wt% and so the experimental conditions mild, there was no decrease in the catalytic activity during 330 min at constant flow rate. In these experimental conditions Co-γAl_2O_3 showed good durability to the hydrolysis of stabilised (5 wt% NaOH) $NaBH_4$ solution. Krishnan et al. [63] proposed a different approach. Extended operation was performed in a 1 L tubular reactor and CoB-Ni was tested in 10 wt% $NaBH_4$ solution for extended duration of up to 60 h. The H_2 generation decreased within 5 min and then it remained almost constant.

From a fundamental point of view, one can understand that in an early stage of investigations the durability tests are secondary. However from an application point of view the durability of the catalyst is as important as its reactivity. Accordingly the durability tests should be systematic and performed in much more severe testing/operating conditions.

3.2.3. *Catalyst shapes*

H_2 generation is expected to be controlled. That is, H_2 must be produced on demand. Depending on whether $NaBH_4$ is stored as solid, gel or aqueous solution the catalyst shape will be different.

If solid $NaBH_4$ is the chosen storage solution, the catalyst structure should not be the critical parameter for the H_2-controlled generation. The amount of water (liquid or vapour) should determine the H_2-controlled generation [35,36]. Using the catalyst either as a powder or supported over a substrate (resin, Ni foam, Cu plate, C cloth or paper, and so on) are two different solutions that can be envisaged. The final choice will depend on the final application.

If $NaBH_4$ gel is used [40], the catalyst has to be water soluble and to be provided with water. At this stage, it appears that the best catalytic solution is metal salt. Homogeneous catalyst may also be considered. Due to the fact that the background is not enough, it is difficult to suggest any other potential (soluble) catalysts. Powder catalysts or metal supported over a substrate do not seem suitable because it is expected that the catalytic site diffuses throughout the gel for catalysing stored $NaBH_4$.

Aqueous (stabilised) solution of $NaBH_4$ is the most investigated storage solution. The studied catalysts were regarded in various forms: powders, pellets and supported over a substrate. Using powder is practical from the one-shot experiment point of view because it is easy to design, to use in small amounts and to stir in aqueous solution. Many catalysts were tested as powder and such experiments permit to obtain reproducible HGRs. However it is difficult to recover, wash and re-use, and this is not practical for durability tests. Now if the application point of view prevails, it is difficult to imagine the utilisation of a powder catalyst. With such form, the go-and-stop utilisation is not conceivable. Indeed to start the hydrolysis of $NaBH_4$ the catalyst powder must be added into the aqueous solution but then it will be impossible to recover the powder catalyst in order to stop the H_2 generation. Actually the more practical option is the catalyst supported over a substrate. Amendola et al. [16,17] suggested the utilisation of a resin for dispersing Ru and such supported catalyst permitted the construction of a prototype. Another examples are the utilisations of either Ni foam for preparing supported cobalt borides [61,62] or Cu substrate for synthesising CoP [73,74]. Though no study deals with their utilisation, monolith and carbon cloth or paper could also be utilised. Note that interestingly Pozio et al. [97] suggested an original solution for utilising a catalyst as a powder. Nevertheless this solution has an inevitable condition. The powder must have iron-magnetic properties, since the reactor is constituted by a magnetic containment. With this prototype, the average hydrogen flow was 0.16 $L(H_2)\ min^{-1}$ during a working time of 15 h while fed with an 8 wt% $NaBH_4$ solution. As the Pozio et al.'s paper [97], several articles [98-101] reported the description of a hydrogen generator. Richardson et al. [99] remarked that the majority of the works utilised batch reactions and suggested an approach that is based on a flow reactor for continuous generation of H_2. Zhang et al. [100] reported a reactor design in which catalyst bed is integrated with a heat exchanger for autothermal operation. With this system, the integrated reactor performances were double than that of a simple reactor and 99 % of the $NaBH_4$ fuel was converted.

Whatever the way of storing $NaBH_4$ and whatever the way of bringing into contact $NaBH_4$ and H_2O, both know-how and engineering should provide solutions in order to bring into contact the catalyst with the system $NaBH_4$-H_2O and to control the H_2 generation. These solutions should make easy the go-and-stop process. In our opinion, there should be no doubt on that.

3.3. Summary

Regarding the efforts devoted to searching for outstanding metal-based catalysts, the global feeling is rather mixed. Whereas highly reactive catalysts have been found, their durability has unfortunately not been assessed. The best catalysts are actually able to generate H_2 at rates high enough for fuelling PEMFCs. However one cannot know if these catalysts can maintain their efficiency and, if they are durable one cannot know how long it will be efficient. The catalysts today investigated suffer from short-lifetime.

Another issue faced by catalysts is the material cost. There are two ways for reducing the material cost. The first is to reduce the content of the expensive, noble metal. The second is to replace the expensive metal by a cost-effective metal like for example Co. As shown in Table 8, the application of both possibilities led to synthesising reactive, less expensive catalysts. There is no doubt that further optimisations will lead to cheaper, active, efficient catalytic materials. Nevertheless a question arises. Which portion of the expense of the complete storage system does the catalyst cost represent? In other words, is the catalyst cost critical for this technology? Unfortunately to our knowledge there is no piece of information that permits to answer the questions.

The way of storing $NaBH_4$ should condition the catalyst shape. Given the state of the art and the current know-how, one may suppose that the catalyst form will not be an issue for implementing the technology.

4. Concluding remarks and other important challenges

4.1. General summary

$NaBH_4$ as hydrogen carrier is today far from being commercialised because it faces several issues. Nevertheless, only two of them are mainly reported throughout the $NaBH_4$-devoted literature. The first main issue is the effective GHSC of either $NaBH_4$ or the system $NaBH_4$-H_2O that is well below the ideal, theoretical value of 10.8 wt%. This issue led the DOE recommending no-go for the aqueous solution of $NaBH_4$ for on-board vehicle application. The second main issue is the efficiency of the catalyst in terms of durability.

Optimising the effective GHSC is intensely investigated (whereas the VHSC is rarely or even never studied). Besides the storage as an aqueous solution, several innovative, original solutions have been proposed: solid $NaBH_4$, $NaBH_4$ gel and utilisation of methanol instead of H_2O. Globally the solutions permitted to improve the effective GHSCs, reaching values up to 7-9 wt%. Capacities above 10 wt% could be reached with further improvements and optimisations. However the value 21 wt% seems somewhat surrealistic. Note that these GHSCs have been calculated only on the basis of the hydrogen carriers $NaBH_4$ and H_2O without taking into consideration the storage system as a whole. The GHSCs for a complete storage system should be much lower than the best values of 7-9 wt%.

A large number of catalysts (acids, metal salts, metal borides, metals, supported metals) were synthesised and assessed. Highly reactive catalysts have been found and these should be capable to generate H_2 for PEMFCs. In other words, one is today able to elaborate catalysts that permit to get adaptable HGRs. However there is today no information about the durability of these catalysts while the durability is a major criterion from an application point of view. Actually the catalysts, even the best ones, suffer from their short lifetime. Regarding the catalyst form, that should be a secondary or even a negligible issue.

4.2. Other challenges

The $NaBH_4$-based H_2 generator is not mature enough for fuelling PEMFCs. Further studies are required for optimising the GHSC and the catalyst efficiency especially in terms of durability. Moreover other important issues also hinder its development. These ones have not been discussed in the previous sections for the reasons evoked in the introduction but one can cite some of them that are in keeping with the chemical reaction $NaBH_4 + (2+x)\ H_2O \rightarrow NaBO_2.xH_2O + 4\ H_2$. For example, Amendola et al. [16] and Wee [12] emphasized it must be admitted that the commercial success of $NaBH_4$ will not be achievable without substantially reducing its cost, which is a significant issue. This has been one of the arguments against $NaBH_4$ when the no-go for automotive applications was announced [29]. One solution for reducing the cost of $NaBH_4$ could be the recycling of the reaction by-products but the recovering and the recycling of the metaborates is currently another significant issue [25]. Even though there are few articles reporting works about the borates recycling (see reviews under ref. [12,24,25]), an intense research within the framework of the DOE programs has been devoted to the recycle of $NaBO_2.xH_2O$ [102]. Such research involved several university groups and companies. Despite innovations, none of the investigated regeneration routes has met the targets in terms of regeneration efficiency, i.e. > 60 wt%, and cost. And the issue of recyclability seems to have played a central role in the no-go decision for the DOE [29]. As another example, one can cite the catalyst recycling issue that is rarely or even never taken into consideration.

The issues tackled in the previous paragraph are related to the catalyzed hydrolysis reaction. However, there are also issues that directly concern the technology from every angle, namely the storage system engineering [103]. Two examples are given hereafter:

- The $NaBH_4$ hydrolysis is highly exothermic and the heat must be managed [103,104]; in fact water acts as a heat sink and the humidified H_2 stream is then hot, which may be detrimental to the fuel cell [105]; moreover overly much water may be detrimental to the storage system if this one is not well designed (e.g. some components could freeze).

- The hydrolysis solid by-products have to be on-board stored till the conversion of all of $NaBH_4$; their storage can be envisaged in a separate bladder tank but several issues have then to be addressed: e.g. the heat of the waste fuel that can favour the $NaBH_4$ hydrolysis, compatibility of the bladder material with the highly basic (pH of 14) waste fuel, and the precipitation of $NaBO_2$ that forms hard crystal clumps that will cause severe abrasion with any pliable bladder material.

Anyway as a conclusion it could be written that further R&D efforts are necessary, at least for niche applications.

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Table 1. Performances of the metal salts.

Salt	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] L(H_2) min^{-1} g^{-1}	Reference
$MnCl_2$	25	1.0	< 49	< 1.2	[15]
$FeCl_2$	25	1.0	65	1.7	[15]
$FeCl_2$	25	0.4	50	1.2	[50]
$CoCl_2$	25	1.0	97	3.7	[15]
$CoCl_2$	25	0.4	50	4.9	[50]
$CoCl_2$	10	0.2	n.i. [d]	0.6	[51]
$CoCl_2$	20	6.8	92	11.4	[38]
$NiCl_2$	25	1.0	99	2.5	[15]
$NiCl_2$	25	0.4	50	2.5	[50]
$NiCl_2$	20	0.2	n.i. [d]	< 0.1	[51]
NiF_2	50	0.2	n.i. [d]	< 0.1	[51]
$CuCl_2$	25	1.0	49	1.2	[15]
$RuCl_3$	25	0.4	50	85.4	[50]
$RhCl_3$	25	0.4	50	85.4	[50]
$PdCl_2$	25	0.4	50	0.1	[50]
$IrCl_4$	25	0.4	50	0.5	[50]
H_2PtCl_6	25	0.4	50	13.3	[50]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in L(H_2) min^{-1} g^{-1}(metal).

[d] n.i.: not informed.

Table 2. Performances of the metal borides.

Boride	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
CoB	20	4.2	n.i. [d]	1.1	[53]
CoB	30	4.2	n.i. [d]	2.8	[53]
CoB	15	0.4	n.i. [d]	3.0	[54]
CoB	25	< 0.1	100	3.3	[56]
CoB	25	< 0.1	100	5.0	[57]
Co_2B	20	0.2	n.i. [d]	< 0.1	[51]
Co_3B	60	1.1	n.i. [d]	6.0	[55]
CoB-Ni	30	4.2	n.i. [d]	11.0	[62]
CoB-Ni	25	1.1	n.i. [d]	1.6	[63]
CoWB-Ni	30	4.2	100	15.0	[65]
CoMnB-Ni	20	1.1	n.i. [d]	n.i. [d]	[61]
NiCoB	28	0.7	100	2.6	[58]
Ni_2B	20	0.2	n.i. [d]	< 0.1	[53]
Ni_3B	60	2.1	n.i. [d]	1.3	[55]
Ni_xB	20	0.3	n.i. [d]	0.3	[33]
Ni_xB	20	0.3	n.i. [d]	0.8	[33]
NiB-SiO_2	25	0.1	n.i. [d]	2.2	[59]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(catalyst).

[d] n.i.: not informed.

Table 3. Performances of the transition and noble metal.

Metal	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
Co powder	20	0.2	n.i. [d]	0.1	[51]
Raney Co	20	0.2	n.i. [d]	0.3	[51]
Co-F	25	n.i. [d]	n.i. [d]	0.4	[72]
CoP-Cu	30	2.1	n.i. [d]	1.0	[73]
CoP-Cu	30	2.1	n.i. [d]	3.3	[74]
Co-PPX-Cl	25	0.5	n.i. [d]	4.3	[75]
Ni powder	20	0.2	n.i. [d]	< 0.1	[51]
Filamentary Ni	30	3.3	n.i. [d]	0.1	[22]
Ni nanoclusters	25	0.1	n.i. [d]	1.7	[71]
Raney Ni	20	0.2	n.i. [d]	0.2	[51]
Raney $Ni_{25}Co_{75}$	20	0.2	n.i. [d]	1.5	[51]
Raney $Ni_{50}Co_{50}$	20	0.2	n.i. [d]	0.7	[51]
Raney $Ni_{75}Co_{25}$	20	0.2	n.i. [d]	1.2	[51]
Ru	25	4.2	n.i. [d]	4.0	[16]
Ru	55	4.2	n.i. [d]	22.0	[16]
Ru	60	1.1	n.i. [d]	18.6	[55]
Ru nanoclusters	25	0.1	70 [e]	2.7	[66]
Ru nanoclusters	25	0.1	70 [e]	1.0	[67]
Ru acetylacetonate	25	0.1	n.i. [d]	1.1	[68]
$Ru_{60}Co_{40}$	25	2.1	n.i. [d]	17.5	[76]
$Ru_{80}Fe_{20}$	25	2.1	n.i. [d]	18.3	[76]
$Ru_{60}Co_{20}Fe_{20}$	25	2.1	n.i. [d]	26.8	[76]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(catalyst).

[d] n.i.: not informed.

[e] The reaction was ceased when 70 % conversion was achieved [66,67].

Table 4. Performances of the $LiCoO_2$ supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
1 wt% Ru-$LiCoO_2$	25	2.1	n.i. [d]	n.i. [d]	[77]
10 wt% Ru-$LiCoO_2$	25	2.1	n.i. [d]	428	[78]
1 wt% Rh-$LiCoO_2$	40	0.5	n.i. [d]	122	[80]
1 wt% Pt-$LiCoO_2$	25	2.1	n.i. [d]	n.i. [d]	[82]
1.5 wt% Pt-$LiCoO_2$	22	4.2	100	203	[27]
10 wt% Pt-$LiCoO_2$	25	2.1	n.i. [d]	300	[78]
15 wt% Pt-$LiCoO_2$	20	0.1	95	367	[81]
10 wt% PtRu-$LiCoO_2$	25	2.1	n.i. [d]	560	[78]
10 wt% PtRu-$LiCoO_2$	25	1.1	100	53	[79]
10 wt% PtRu-Co_3O_4	25	1.1	100	85	[79]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

Table 5. Performances of the C supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
9 wt% Co-C	30	0.2	100	0.2	[30]
10 wt% Co-C	20	1.1	100	136	[84]
1 wt% Ru-C	40	0.1	n.i. [d]	0.7	[87]
2 wt% Ru-C	20	0.3	n.i. [d]	35	[33]
5 wt% Ru-C	25	0.2	n.i. [d]	13.6	[85]
10 wt% Ru- CF [e]	20	2.1	n.i. [d]	14.2	[76]
1 wt% Rh-C	40	0.1	n.i. [d]	1.1	[87]
1 wt% Pd-C	40	0.1	n.i. [d]	0.1	[87]
10 wt% Pd-C	23	< 0.1	100	< 0.1	[86]
1 wt% Pt-C	40	0.1	n.i. [d]	0.7	[87]
1 wt% Pt-C	20	0.4	98	2.9	[89]
2 wt% Pt-C	30	1.1	64	5.0	[84]
20 wt% Pt-C	20	2.1	100	115.0	[83]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

[e] CF : Carbon Fibers.

Table 6. Performances of the metal oxide supported metals.

Supported catalyst	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] L(H_2) min^{-1} g^{-1}	Reference
9 wt% Co-γAl_2O_3	30	0.2	100	1.0	[30]
9 wt% Co-γAl_2O_3	30	3.2	100	2.4	[30]
1 wt% Rh-γAl_2O_3	40	0.1	n.i. [d]	0.4	[87]
2 wt% Ru-γAl_2O_3	30	2.5	70 [e]	4.8	[92]
1 wt% Pt-γAl_2O_3	40	0.1	n.i. [d]	0.2	[87]
2 wt% Pt-γAl_2O_3	30	1.1	81	2.9	[90]
1 wt% Ru-TiO_2	20	0.4	n.i. [d]	15.6	[94]
1 wt% Ru-TiO_2	40	0.1	n.i. [d]	1.6	[87]
1 wt% Rh-TiO_2	40	0.1	n.i. [d]	3.0	[87]
1 wt% Pd-TiO_2	40	0.1	n.i. [d]	0.2	[87]
1 wt% Pt-TiO_2	40	0.1	n.i. [d]	1.4	[87]
1 wt% Pt-TiO_2	20	0.4	n.i. [d]	3.7	[94]
2 wt% Pt-TiO_2	20	0.4	n.i. [d]	4.8	[93]
2 wt% Pt-ZrO_2	20	0.4	n.i. [d]	2.1	[93]
1 wt% Ru-ZrO_2-SO_4^{2-}	20	0.4	98	10.5	[89]
1 wt% Pt-ZrO_2-SO_4^{2-}	20	0.4	n.i. [d]	0.3	[89]
2 wt% Pt-ZrO_2-SO_4^{2-}	20	0.4	n.i. [d]	2.4	[93]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in L(H_2) min^{-1} g^{-1}(metal).

[d] n.i.: not informed.

[e] The reaction was ceased when 70 % conversion was achieved [97].

Table 7. Performances of the supported alloys.

Supported alloys	Temperature °C	GHSC [a] wt%	Yield [b] %	HGR [c] $L(H_2)\ min^{-1}\ g^{-1}$	Reference
1.4 wt% PtPd-CNT [e]	29	< 0.1	100	9.0	[91]
16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-CF [f]	20	2.1	n.i. [d]	41.7	[76]
13.3 wt% $Ru_{75}Co_{25}$-CF [f]	20	2.1	n.i. [d]	37.1	[76]
1 wt% RuCu-TiO_2	20	0.4	n.i. [d]	3.1	[94]
1 wt% RuPd-TiO_2	20	0.4	n.i. [d]	6.0	[94]
1 wt% Ru_2Pt_1-TiO_2	20	0.4	n.i. [d]	15.2	[94]
1 wt% RuPt-TiO_2	20	0.4	n.i. [d]	10.0	[94]
1 wt% Ru_1Pt_2-TiO_2	20	0.4	n.i. [d]	10.0	[94]
1 wt% RuAg-TiO_2	20	0.4	n.i. [d]	3.9	[94]
2 wt% PtPd-TiO_2	20	0.4	n.i. [d]	4.2	[93]
2 wt% PtIr-TiO_2	20	0.4	n.i. [d]	3.2	[93]
1 wt% PtAg-TiO_2	20	0.4	n.i. [d]	2.6	[94]
2 wt% PtAg-TiO_2	20	0.4	n.i. [d]	2.6	[93]
10 wt% PtRu-Co_3O_4	25	1.1	100	85.0	[79]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

[b] Yield used to calculate the HGR.

[c] HGR: Hydrogen Generation Rate, in $L(H_2)\ min^{-1}\ g^{-1}$(metal).

[d] n.i.: not informed.

[e] CNT: Carbon NanoTubes.

[f] CF : Carbon FIbers.

Table 8. Reachable power levels at about room temperature for the best catalysts given in Tables 1 to 7.

Catalyst	GHSC [a] wt%	Mass for 100 W [b] g	Power for 1 g(metal) [c] W	Reference
$CoCl_2$	6.8	0.088	1140	[38]
CoB	4.2	0.909	110	[53]
CoB-Ni	4.2	0.091	1100	[62]
CoWB-Ni	4.2	0.067	1500	[65]
CoP-Cu	2.1	1.000	100	[73]
Ru	4.2	0.250	400	[16]
$Ru_{60}Co_{40}$	2.1	0.057	1750	[76]
$Ru_{80}Fe_{20}$	2.1	0.055	1830	[76]
$Ru_{60}Co_{20}Fe_{20}$	2.1	0.037	2680	[76]
10 wt% Ru-$LiCoO_2$	2.1	0.002	42800	[78]
1.5 wt% Pt-$LiCoO_2$	4.2	0.005	20300	[27]
10 wt% Pt-$LiCoO_2$	2.1	0.003	30000	[78]
10 wt% PtRu-$LiCoO_2$	2.1	0.002	56000	[78]
10 wt% Ru-CF	2.1	0.070	1420	[76]
20 wt% Pt-C	2.1	0.009	11500	[83]
9 wt% Co-γAl_2O_3	3.2	0.417	240	[30]
2 wt% Ru-γAl_2O_3	2.5	0.021	4800	[92]
16.6 wt% $Ru_{60}Co_{20}Fe_{20}$-CF	2.1	0.024	4170	[76]
13.3 wt% $Ru_{75}Co_{25}$-CF	2.1	0.027	3710	[76]

[a] GHSC: Gravimetric Hydrogen Storage Capacity, according to the given experimental conditions.

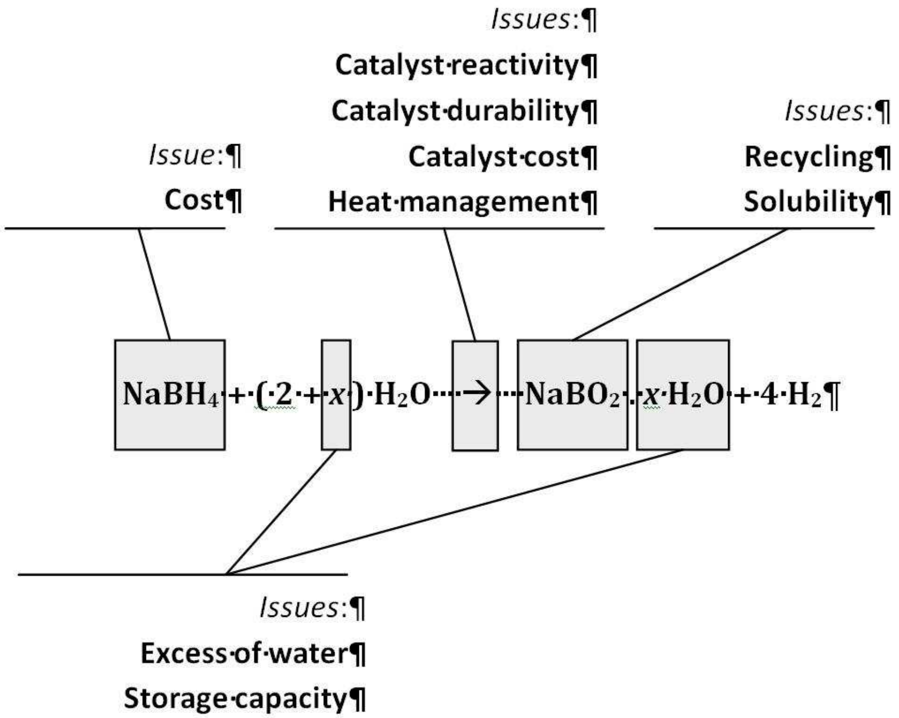
[b] Mass of metal (active phase) for powering a 100 W fuel cell [16].

[c] Power level of a H_2-powered PEMFC when 1 g of metal (active phase) generates H_2 from $NaBH_4$.

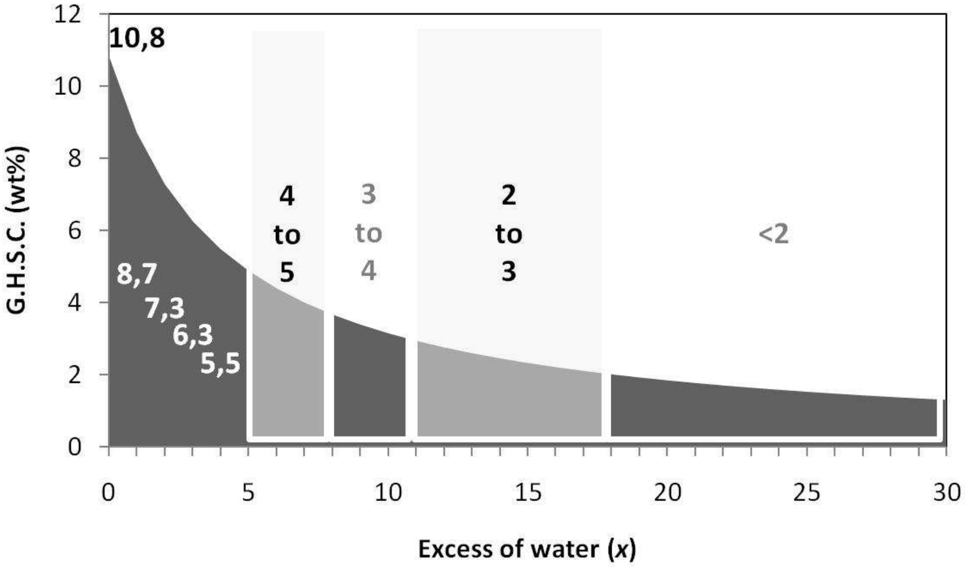
Figure 1. Catalysed hydrolysis of sodium borohydride: a reaction full of issues.

Figure 2. Evolution of the gravimetric hydrogen storage capacity (G.H.S.C. in wt%) of the fuel [$NaBH_4$+(2+x)H_2O] with the excess of water (x).

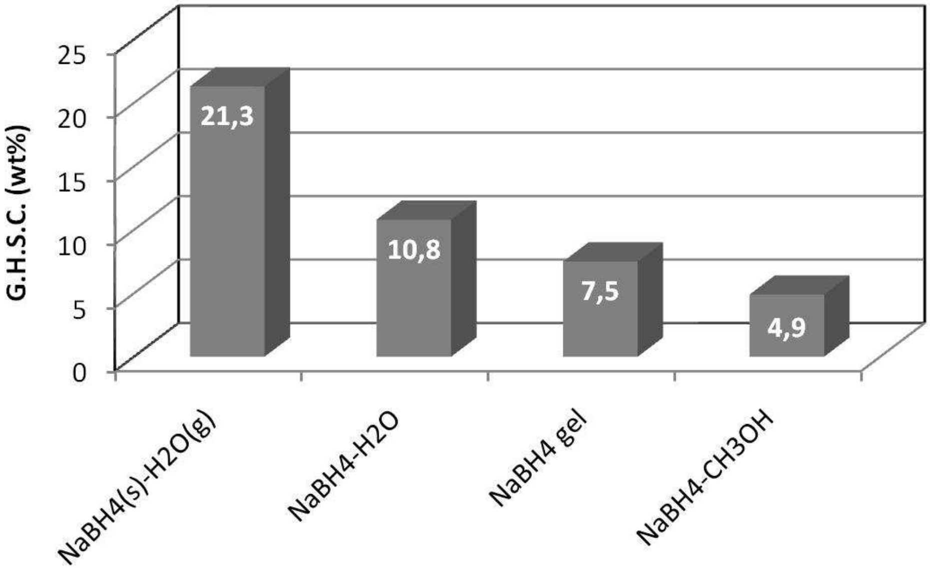
Figure 3. Ideal gravimetric hydrogen storage capacity of the $NaBH_4$ storage solutions.



Catalysed hydrolysis of sodium borohydride: a reaction full of issues.
225x169mm (120 x 120 DPI)



Evolution of the gravimetric hydrogen storage capacity (G.H.S.C. in wt%) of the fuel [$NaBH_4$+(2+x)H_2O] with the excess of water (x).
246x146mm (120 x 120 DPI)



Ideal gravimetric hydrogen storage capacity of the NaBH4 storage solutions.
235x144mm (120 x 120 DPI)