Review

A review: Hydrogen generation from borohydride hydrolysis reaction

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A B S T R A C T

In this review, a convenient hydrogen generation technology based on sodium borohydride and water as hydrogen carriers has been summarized. The recent progresses in the development of the hydrogen generation from sodium borohydride hydrolysis are reviewed. The NaBH$_4$ hydrolysis behavior is discussed in detail. From reported results, it is considered that hydrogen generation from sodium borohydride hydrolysis is a feasible technology to supply hydrogen for the PEMFC. It has been found that the reported results are encouraging although there are some engineering problems that lie ahead. The critical issues of this hydrogen generation technology have been highlighted and discussed.

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Contents

1. Introduction

It is known that hydrogen is a clean energy carrier. Hydrogen releases energy with high efficiency through electro-oxidation reaction in a fuel cell to generate only product: water. Hydrogen can be stored in the form of molecular hydrogen in pressurized vessels [1–3], liquefied hydrogen tanks [4,5] and carbon materials [4–12]. It also can be stored in the form of atomic hydrogen in metal hydrides

(MH) [13] or in the form of hydride ion in protide compounds such as alanetes (MAlH$_4$) [14–17] and borohydrides (MBH$_4$) [18–23]. Metal hydrides generate hydrogen by thermal decomposition and they are considered reproducible in reversible manners. However, their hydrogen capacities are lower than protide compounds as shown in Table 1 [24]. Some Mg-based alloys have higher hydrogen capacities, but the high temperature requirement for releasing hydrogen limits their practical uses as hydrogen storage materials. High air sensitivity is another issue of these compounds.

Sodium borohydride (NaBH$_4$) is one of the borohydrides. It is stable in dry air, and is easily handled like common chemicals compared with other hydrogen storage materials. Generating H$_2$

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Table 1
Comparison of hydrogen capacity in metal hydrides and protide compounds [24].

	Metal hydride						Protide compound	
Typical metal hydride	AB_5H_6 $LaNi_5H_6$	AB_2H_4 $ZrMn_2H_{3.46}$	ABH_2 $TiFeH_{1.9}$	A_2BH_4 Mg_2NiH_4	AH_x MgH_2	M^IAlH_4 $NaAlH_4$	M^IBH_4 $LiBH_4$ $NaBH_4$	$M^{III}(BH_4)_3$ $Al(BH_4)_3$
H-capacity (wt.%)	1.4	1.7	1.8	3.6	7.6	7.4	18.4 10.6	16.8

catalytically from $NaBH_4$ solutions has many advantages: $NaBH_4$ solutions are nonflammable; reaction products are environmentally benign; rate of H_2 generation is easily controlled; the reaction product $NaBO_2$ can be recycled; H_2 can be generated even at low temperatures. The theoretical hydrogen amount released is 10.8 wt.% by $NaBH_4$ hydrolysis reaction and half of hydrogen is from H_2O. The $\Delta H°$ values of reactions (1), (4) and (5) were calculated from the standard enthalpy of formation (298.15 K) [106]:
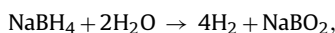
$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2,$$
$$\Delta H° = -216.7 \, kJ \, mol^{-1} NaBH_4 \tag{1}$$

Furthermore, the gravimetric capacity of $NaBH_4$ is higher than that of metal hydrides and the volumetric capacity of $NaBH_4$ is higher than that of compressed and liquefied hydrogen. For a power generation system based on the proton exchange membrane fuel cell (PEMFC) using hydrogen as the fuel from $NaBH_4$ hydrolysis, some water from the PEMFC can be reused for $NaBH_4$ hydrolysis. Then, the total reaction can be described as:

$$NaBH_4 + O_2 = NaBO_2 + 2H_2O \tag{2}$$

Due to these merits mentioned above, hydrogen generation from $NaBH_4$ hydrolysis has attracted many attentions. The application feasibility of $NaBH_4$ as the hydrogen generation resource has been studied [25–28]. Wee et al. [29] introduced and discussed some research achievements on the use of H_2 generated via the $NaBH_4$ hydrolysis reaction for PEMFCs.

In this review, $NaBH_4$ hydrolysis behavior is summarized in details. Recent progresses in the development of hydrogen generation technology from $NaBH_4$ hydrolysis are reviewed. The critical issues of this emerging hydrogen generation technology have been highlighted and discussed.

2. BH_4^- hydrolysis reaction

Early in the 1950s, Schlesinger et al. [18] suggested using $NaBH_4$ to generate hydrogen at ambient conditions. It was reported that $NaBH_4$ solution released 90% of the stoichiometric amount of hydrogen from the hydrolysis reaction. Through isotope analysis of deuterium (D), Pecsok investigated the BH_4^- hydrolysis behavior catalyzed by H^+ [30]. It was found that BH_4^- would react with H^+ to form a transient of BH_5. BH_5 would split into BH_3 and H_2. Then BH_3 would react with H_2O to form H_3BO_3 and H_2 as shown in
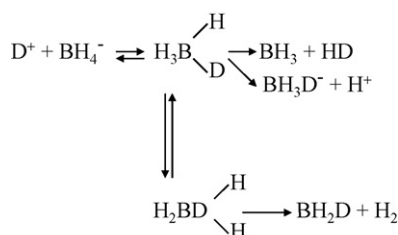

Fig. 1. Schematic BH_4^- hydrolysis behavior when catalyzed by H^+ [30].
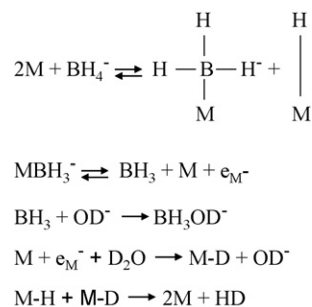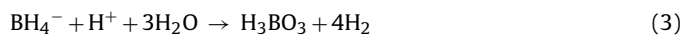

Fig. 2. Schematic BH_4^- hydrolysis behavior when catalyzed by metallic catalysts [26].

Fig. 1. The BH_4^- hydrolysis reaction could be described as:

$$BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 4H_2 \tag{3}$$

Hydrogen generation rate was proportional to the concentration of BH_4^- and pH value of the BH_4^- solution. Keçeli and Özkar suggested using a highly active homogeneous catalyst: $Ru(acac)_3$ as the catalyst for $NaBH_4$ hydrolysis. The $Ru(acac)_3$ catalyzed hydrolysis of $NaBH_4$ was first order with respect to both catalyst and $NaBH_4$ [31].

Kaufman and Sen investigated the BH_4^- hydrolysis behavior catalyzed by heterogeneous catalysts: Co, Ni (or Raney Ni) [26]. It was found that the disassociative adsorption of BH_4^- ion would occur on the catalyst M (M = Co, Ni) as shown in Fig. 2. Metallic catalyst would transfer electrons to the molecular H_2O to generate hydrogen. The effect of these transition metals was characterized by zero-order kinetics. Associative desorption of absorbed hydrogen was another path of hydrogen generation. The transient of BH_3OH^- would stepwisely reacted with OH^- to form hydrogen and $B(OH)_4^-$. A nuclear magnetic resonance (NMR) spectroscopy-monitored experiment proved the existence of the $(BH_3OH)^-$ anion as an individual species in solutions [32]. Edwards et al. found that meta-borate ion existed in the form of $B(OH)_4^-$ not BO_2^- in aqueous solutions [33]. Metin and Özkar studied the nickel(0) nanocluster-catalyzed hydrolysis of $NaBH_4$ with low concentration [35]. It was found that BH_4^- hydrolysis followed first-order reaction in catalyst concentration and zero order in $NaBH_4$ concentration. The hydrogenphosphate-stabilized nickel(0) nanoclusters provided a lower activation energy than bulk nickel for the hydrolysis of $NaBH_4$. Guella et al. conducted detailed kinetic analyses of the Pt catalyzed $NaBH_4$ hydrolysis in alkaline media by ^{11}B NMR [36]. The reaction kinetics was found to be of first-order in catalyst and zero order in borohydride. Based on Langmuir–Hinshelwood model, a unified kinetic model was suggested [37]. The results indicated that the reaction consisted of two important steps: the adsorption of BH_4^- on the surface of the catalyst and the reaction of the adsorbed species on the catalyst surface.

Ingersoll et al. investigated the influence of NaOH concentration in $NaBH_4$ solutions on the hydrogen generation rate when using nickel–cobalt–boride (Ni–Co–B) as the catalyst [38]. The hydrogen generation rate increased for lower NaOH concentrations in the alkaline $NaBH_4$ solution then decreased after reaching a maximum at 15 wt.% of NaOH. The hydrogen generation rate was found to be
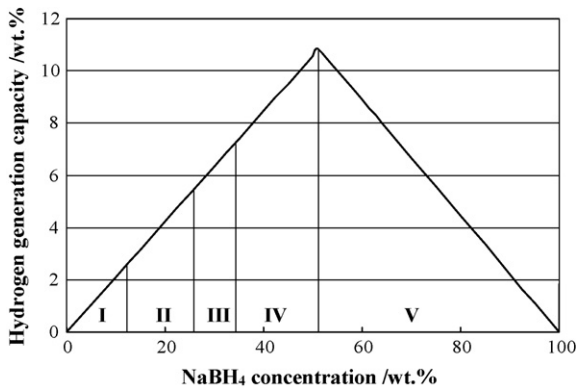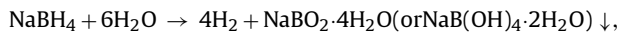
Fig. 3. Influence of NaBH$_4$ concentration on the hydrogen generation capacity based on stoichiometric calculation from NaBH$_4$ hydrolysis reaction.

constant with respect to the concentration of NaBH$_4$. Zhang et al. studied the kinetics of catalytic hydrolysis of alkaline BH$_4^-$ solutions for a Ni-metal supported catalyst over a temperature range from 0 to 30 °C and a NaBH$_4$ concentration range from 1.34 to 5.44 M [39]. It was reported that BH$_4^-$ hydrolysis reaction rate was dependent upon concentration of NaBH$_4$, NaOH and H$_2$O. The intrinsic kinetics model revealed the importance of water management for operation of a NaBH$_4$-based system for hydrogen storage and generation.

The concentration of NaBH$_4$ should be as high as possible in order to improve the fuel energy density. However, when the NaBH$_4$ concentration was high enough, hydrated borates as the reaction product would precipitate from the solution, which would block the active sites of the catalysts and bring about the complexity of solution transportation. On the other hand, H$_2$O reactivity would influence the hydrolysis reaction mechanism as H$_2$O was another hydrogen source for the BH$_4^-$ hydrolysis. Theoretically speaking, with decreasing the water content in the reaction system, following hydrolysis reactions would occur:

$$NaBH_4 + 6H_2O \rightarrow 4H_2 + NaBO_2 \cdot 4H_2O(orNaB(OH)_4 \cdot 2H_2O) \downarrow,$$

$$\Delta H^\circ = -272.4 \, kJ \, mol^{-1} NaBH_4 \tag{4}$$

$$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaBO_2 \cdot 2H_2O(orNaB(OH)_4) \downarrow,$$

$$\Delta H^\circ = -250.1 \, kJ \, mol^{-1} NaBH_4 \tag{5}$$

Fig. 3 shows the influence of NaBH$_4$ concentration (or H$_2$O addition amount) on the hydrogen generation capacity based on the stoichiometric calculation of reactions of (1), (4) and (5). Table 2 lists the phase compositions after NaBH$_4$ hydrolysis reaction corresponding to the initial NaBH$_4$ concentration. Shang and Chen reported that not only NaOH concentration, NaBH$_4$ concentration but also the byproduct (sodium meta-borate) would influence the hydrogen generation rate when using concentrated alkaline NaBH$_4$ solutions. The hydrolysis of NaBH$_4$ was first order to the concentration of NaBH$_4$ [40,41].

Table 2
The hydrogen generation capacities and phase compositions after NaBH$_4$ hydrolysis reaction corresponding to the initial NaBH$_4$ solution.

	NaBH$_4$ concentration (wt.%)	Phase composition	Hydrogen generation capacity (wt.%)
I	0–12.3	L	0–2.6
II	12.3–25.9	L + NaB(OH)$_4$·2H$_2$O	2.6–5.5
III	25.9–34.4	NaB(OH)$_4$·2H$_2$O + NaB(OH)$_4$	5.5–7.3
IV	34.4–51.2	NaB(OH)$_4$ + NaBO$_2$	7.3–10.8
V	51.2–100	NaBO$_2$ + NaBH$_4$	10.8–0

Table 3
Various kinetic studies of H$_2$ generation via NaBH$_4$ hydrolysis reaction.

NaBH$_4$/NaOH concentration	Rate equation	Temperature (°C)	Catalyst		Active energy (kJ mol^{-1})	References
0.001 M/0 M	$-d[BH_4^-]/dt = k[BH_4^-][H^+]$	15–35	Homogeneous catalyst	H$^+$		[30]
0.15 M/0 M	$-d[BH_4^-]/dt = k[BH_4^-][Ru]$	20–45		Ru(acac)$_3$	58.2	[31]
0.005 M/0 M	$-d[BH_4^-]/dt = k$	22		Co powder	75	[26]
0.005 M/0 M	$-d[BH_4^-]/dt = k$	22		Ni powder	71	[26]
0.005 M/0 M	$-d[BH_4^-]/dt = k$	22		Raney Ni	65	[26]
0.04–0.2 M/0 M	$-4d[NaBH_4]/dt = d[H_2]/dt = k[Ru]$	25–45	Heterogeneous catalyst	Ru	28.5	[105]
0.1–0.2 M/0.1 M	$-d[BH_4^-]/dt = k_{true}[H_2O][Pt]$	25		Pt/C	45	[36]
0.15 M/0 M	$-4d[NaBH_4]/dt = d[H_2]/dt = k[Ni]$	25–45		Ni cluster	54	[35]
1.3 M/3.75 M	$d[H_2]/dt = k_0 \exp(-Ea/RT)$	8–27		Ni–Co–B	62	[38]
5.73 M/1.9 M	$-4d[NaBH_4]/dt = d[H_2]/dt = k$	25–55		Ru/resin	47	[34]
1.34–5.44 M/0.26–1.9 M	$-d[NaBH_4]/dt = k[NaBH_4]^{-0.41}[NaOH]^{0.13}[H_2O]^{0.68}$	0–30		Ni/metal	52	[39]
1.32–5.28 M/0–2.5 M	$d[H_2]/dt = k[BH_4^-]/(1 + k_1[NaOH])$	26–60		Ru/C	37.3	[41]

It was reported that the BH_4^- hydrolysis followed zero-order reaction at low temperatures but the first-order behavior at higher temperatures on carbon-supported Ru catalyst [37]. As pointed out by Moon et al., temperature is a major parameter that affected the solubility of $NaBO_2$ [42]. If the hydrolysis temperature is over the melting point of $NaB(OH)_4 \cdot 2H_2O$, $NaB(OH)_4$ would be formed when a $NaBH_4$ solution with $NaBH_4$ concentrations from 25.9 to 34.4 wt.% is used for hydrogen generation. However, if the hydrolysis temperature is controlled under the melting point of $NaB(OH)_4 \cdot 2H_2O$, some unreacted $NaBH_4$ would remain due to the mass transport barrier of formed $NaB(OH)_4 \cdot 2H_2O$ phase.

Table 3 summarizes the kinetic studies on the $NaBH_4$ hydrolysis reaction models when using solutions with different concentrations of $NaBH_4$ for hydrogen generation. From these results, it can be concluded that hydrogen generation follows first-order reaction with respect to both $NaBH_4$ concentration and catalyst concentration when using homogeneous catalysts for BH_4^- hydrolysis. When using heterogeneous catalysts for BH_4^- hydrolysis, zero-order kinetics dominates at low concentration of $NaBH_4$ but first-order kinetics at high concentration of $NaBH_4$.

It is known that 1 mole of $B(OH)_4^-$ will be formed after 1 mole of BH_4^- is hydrolyzed. It means that 2 moles of free H_2O are localized by BO_2^- ions, which results in decreasing H_2O reactivity. As a result, BH_4^- hydrolysis would be dominated by the H_2O diffusion process. Therefore, hydrogen generation rate are dependent upon the $NaBH_4$ concentration and H_2O concentration if high concentrated $NaBH_4$ solutions are applied for hydrogen generation. However, some results showed that $NaBH_4$ concentration would influence the hydrogen generation rate even if $NaBH_4$ solutions with low concentrations were used [39,43,44]. Probably, it could be attributed to the applied catalyst and used catalyst amount because both of them would influence the BH_4^- hydrolysis behavior.

Use of solid $NaBH_4$ rather than alkaline BH_4^- solutions was considered to be another way to produce hydrogen with high energy density by increase of the H_2O utilization. Liu et al. investigated the hydrolysis reaction by starting with solid $NaBH_4$ and adding less amount of water in an attempt to explore the maximum hydrogen generation capacity [45]. The hydrogen generation capacity could reach up to 7 mass% through reaction (5). Matthews and co-workers studied the steam hydrolysis of $NaBH_4$. It was found that hydrated meta-borate: $NaB(OH)_4$ was produced after hydrogen generation [46]. The hydration degree of the meta-borate was closely tied to the amount of water in the reaction (5). It was reported that unlike the reaction in liquid water, up to 95% yield of hydrogen could be obtained with pure steam without a catalyst [47].

3. Catalyst for BH_4^- hydrolysis

3.1. Homogeneous catalyst

Since Schlesinger et al. [18] found that the $NaBH_4$ hydrolysis reaction could be significantly accelerated by addition of acids, few investigations on homogeneous catalysts have been carried out due to the difficulty of the reaction process controlling. Recently, Keçeli and Özkar [31] suggested using ruthenium(III) acetylacetonate as the homogeneous catalyst for $NaBH_4$ hydrolysis reaction [30]. It is considered that use of homogeneous catalyst for $NaBH_4$ hydrolysis is good for continuous hydrogen production but not suitable for the hydrogen supply on demand because $NaBH_4$ hydrolysis reaction usually become uncontrollable due to the difficulty to halt reaction process.

3.2. Heterogeneous catalyst

It was known that hydrogen was released only when alkaline $NaBH_4$ solutions passed over the solid catalyst surface, so that the flow rate of the solution over the catalyst could control the rate of hydrogen generation. This allowed hydrogen generation to be matched to hydrogen consumption in the fuel cell. Xia and Chan suggested another controlling manner by which the hydrogen generation can be controlled by inserting or removing the catalyst into/from the solution [72]. Therefore, use of heterogeneous catalysts was considered to be one of the methods to control $NaBH_4$ hydrolysis reaction. It was reported that hydrogen generation rate was easy to be controlled by using heterogeneous catalysts [26]. Cobalt and nickel borides were the most investigated catalysts [18,19,21,22,26,36,48]. Eom et al. studied the cobalt–phosphorous (Co–P) catalysts by electroless deposition. It was found that Co–P catalysts with finer crystalline Co exhibited a higher hydrogen generation rate [49]. Co and Co–P catalysts can be prepared by electroplating on Cu in sulphate-based solution without or with an addition of $H_2PO_2^-$ ions [50].

Dong et al. studied the effect of heat treatment of nickel boride catalyst (Ni_xB) on the catalysis of $NaBH_4$ hydrolysis reaction. It was found that the Ni_xB catalyst showed great improvements in catalytic activity and operation stability after heat treatment at 150 °C in vacuum [51]. The Co–B catalyst treated at 500 °C exhibited very good catalytic activity [52].

Suda et al. studied the catalytic properties of some intermetallic compounds such as Mg_2Ni and its hydride [23,53]. Kim and co-workers developed Ru60Co20Fe20 alloy as the $NaBH_4$ hydrolysis catalyst [54]. Some other alloys of precious metals such as RuM (M = Cu, Pd, Ag, Pt), PtAg were suggested by Demirci and Garin [55]. It was found that alloying Ru with Pt demonstrated the same cat-
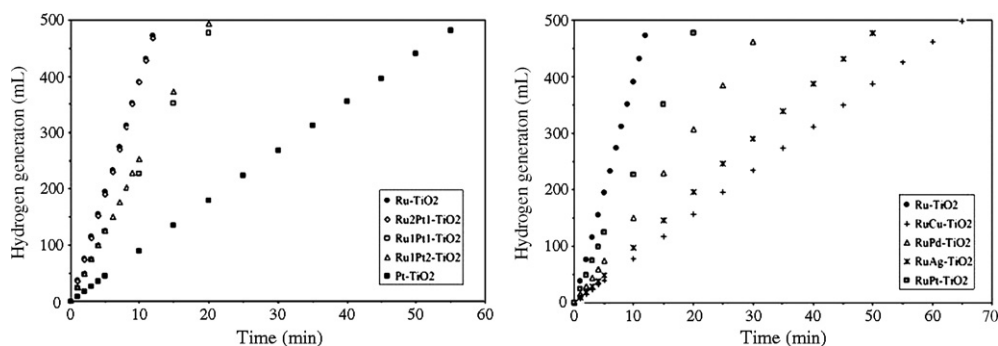

Fig. 4. Volume of hydrogen generated as a function of time for the TiO_2-supported catalysts [55].
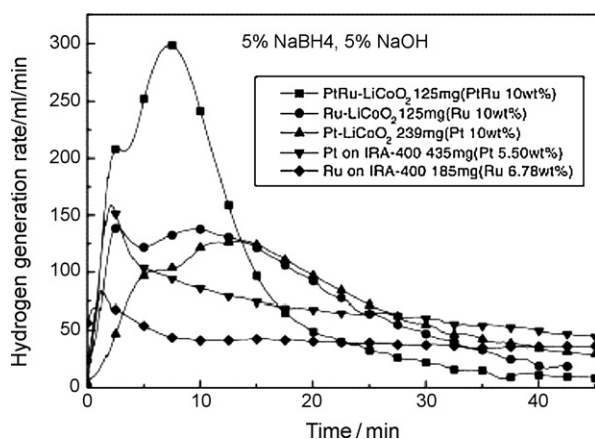
Fig. 5. Hydrogen generation with different catalysts in 5 wt.% NaBH$_4$ (5 wt.% NaOH) solution [64].

alytic activity as Ru, but alloying with inactive metals like Cu, Pd or Ag deteriorated the performances of Ru as shown in Fig. 4.

In order to improve the catalyst dispersion, carbon-supported catalysts were developed to obtain high catalytic activity. For examples, Ru/C [41] and carbon-supported platinum (Pt/C) catalysts [56–59] exhibited excellent hydrogen generation rates. Carbon-supported Co–B catalysts also can be prepared by impregnation–chemical reduction method [60]. Pena-Alonso et al. suggested using carbon nanotube (CNT)-supported Pt and Pd as the catalysts [61].

It was reported that the hydrogen generation rates when using Pt–LiCoO$_2$ catalyst were high compared with those using other metal and metal oxide [62]. In a closed pressure vessel, NaBH$_4$ hydrolysis on Pt–LiCoO$_2$ catalyst would drastically increase the pressure owing to the generation of large quantities of hydrogen gas by synergism of hydrogen pressure and the catalyst [63]. Krishnan et al. compared the hydrogen generation kinetics using IRA-400 anion resin dispersed Pt, Ru catalysts and LiCoO$_2$-supported Pt, Ru and PtRu catalysts [64]. It was found that the performance of the LiCoO$_2$-supported catalysts was better than that of ion-exchange resin dispersed catalysts as shown in Fig. 5. Several synthesis methods of LiCoO$_2$-supported catalyst such as microwave-assisted polyol process [65], sintering [66] were suggested. Krishnan et al. [67] found that the catalytic activity of LiCoO$_2$ was due to the formation of cobalt boride (CoB) by the reduction of LiCoO$_2$ by NaBH$_4$. The performance of Co$_3$O$_4$ and LiCoO$_2$ was comparable to various noble metal catalysts. Liu et al. confirmed that a small percentage of cobalt existed in the metallic form after hydrogen generation by using LiCoO$_2$-supported Pt or Ru as the catalyst [66].

It is considered that NaBH$_4$ is a strong reducing agent. Many metallic catalysts mentioned above can be obtained by adding precursor solution into solid NaBH$_4$ or NaBH$_4$ solutions. For examples, ruthenium(0) nanoclusters could be prepared from the reduction of RuCl$_3$·3H$_2$O and stabilized by using acetate ion [68]. Co–B catalyst could be prepared by using different precursors (CoCl$_2$ and CoSO$_4$) [69]. The synthesis methods of Ni$_3$B, Co$_3$B, and Ru catalysts were also reported [70]. It was reported that the H$_2$O amount in precursor solution was very important especially when solid NaBH$_4$ or NaBH$_4$ gel was applied for NaBH$_4$ hydrolysis [45,71].

4. Catalyst support technology

It was known that generated hydrogen bubbles through NaBH$_4$ hydrolysis would move catalyst powders all around. Therefore, applied catalysts should keep a certain shape and be fixed in practical uses. Amendola et al. [34] suggested use of the ion-exchange

resin beads as the catalyst support. Yi and co-workers suggested using γ-Al$_2$O$_3$ as a support material. It was found that Co/γ-Al$_2$O$_3$ had quick response and good durability to the hydrolysis of alkaline NaBH$_4$ solution [73]. It was reported that TiO$_2$ [55,74,75], solid acid sulphated-zirconia [43,76] and silica [77] could be used as support materials of metal catalysts.

It was considered that using sponge material as a catalyst substrate can effectively decrease the flow resistance of hydrogen stream. Lee and co-workers suggested loading Ni or Co catalyst into Ni foam to make a catalyst sheet using stylene–butadiene–rubber (SBR) as a binding material [78]. An investigation of durability characteristics of a pasted filamentary Ni catalyst was performed and extensive approaches for elucidating the degradation mechanism of the catalyst were undertaken. It was found that agglomeration of catalyst resulted in a reduction of specific surface area. The borate film formed on the catalyst was another reason for deteriorated catalysts [79]. A chemical reduction of Co precursors coated on a Ni foam support was also suggested [80]. It was found that the catalyst showed a maximum activity to hydrogen generation when annealing at approximately 250 °C. Adhesion of the catalyst to the support could be enhanced by heat treatment at 300–400 °C. Dai et al. [81] developed a modified electroless plating method to prepare amorphous Co–B catalyst supported on Ni foam. Compared to the conventional electroless plating method, the suggested method was more effective and the produced Co–B catalyst had higher catalytic activity. The catalytic activity of the supported Co–B catalyst was highly dependent upon the plating times and calcination conditions.

5. Hydrogen generation system

Based on the achievements in catalyst development, several hydrogen generation systems have been constructed in different scales. Prosini and Gislon [82] designed a small hydrogen generation system for a fuel cell to power a cellular phone. The device was to satisfy the hydrogen supply on demand at room temperature and pressure as shown in Fig. 6. The hydrogen capacity was as high as 2.5% (w/w). By converting this amount of hydrogen to electricity by a fuel cell working at 0.8 V, it is possible to achieve a system energy density of about 720 W h kg^{-1}, four times larger than commercial high energy density lithium-ion batteries.

In portable applications, power generation devices should be placed in all directions without orientation preference. However, when using a liquid fuel to power a fuel cell, a system orientation problem would occur as the fuel supply system has to be placed in some special directions, which would cause inconvenience in use. Gervasio et al. [83] designed an orientation-independent hydrogen
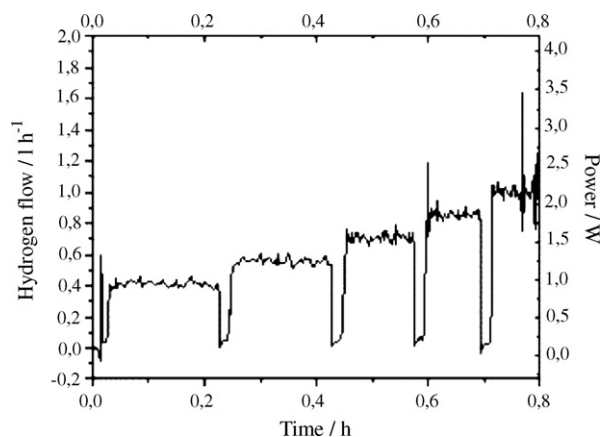

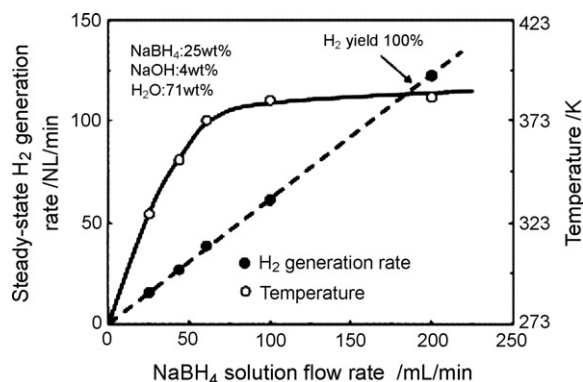**Fig. 6.** Hydrogen response measurement of the designed system [82].

Fig. 7. Influence of NaBH$_4$ solution flow rate on steady-state H$_2$ generation rate [86].

generator operating at ambient conditions. The hydrogen generator could provide power output of about 10 W, in which a membrane kept liquid in the reactor, but allowed hydrogen gas to pass out of the reactor. Kim et al. built an integrated system of hydrogen generation system using Co–B catalyst supported on nickel foam, and a PEMFC stack. Power output of about 465 W was achieved at a constant loading of 30 A [84]. Patel et al. reported that the maximum H$_2$ generation rate of about 5 L min^{-1} g^{-1} of catalyst could be achieved by using thin film Co–B catalyst. The H$_2$ generation rate could power a PEMFC with output of 0.9 kW operating at 0.7 V [85]. Kojima et al. developed a hydrogen generator using a Pt–LiCoO$_2$-coated honeycomb monolith [86]. The gravimetric and the volumetric H$_2$ densities of the system reached 2 wt.% and 0.15 kg H$_2$ m^{-3}, respectively. The hydrogen generator successfully provided a maximum H$_2$ generation rate of 120 NL min^{-1} corresponding to 12 kW output for a standard PEMFC operating at 0.7 V as shown in Fig. 7.

BH$_4{}^-$ hydrolysis is an exothermic reaction. It was observed that temperature had a significant effect on the rate of reaction during operation [87]. Zhang et al. [88] suggested a hydrogen storage system whose dynamic reactor startup and response characteristics were rather satisfactory at various hydrogen demand conditions. The catalyst reactor was operated without need of fuel preheating. Catalyst durability of more than 700 h was demonstrated. Later, they developed a novel reactor in which catalyst bed was integrated with a heat exchanger for auto thermal operation [89]. Over 200% enhancement in reactor throughput was achieved as shown in Fig. 8.

6. Other borohydrides

Besides NaBH$_4$, other borohydrides such as LiBH$_4$, KBH$_4$ were attempted to be used for hydrogen generation through hydrolysis
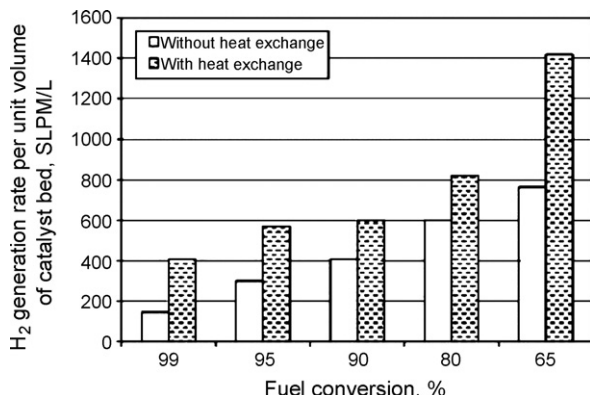

Fig. 8. Reactor performance with and without heat exchange [89].

reaction. It was reported that the gravimetric and the volumetric hydrogen densities peaked at a certain concentration of LiBH$_4$. The gravimetric hydrogen density per unit weight of LiBH$_4$ and H$_2$O could reach up to 7.4 wt.%, volumetric hydrogen density per unit weight of NaBH$_4$ and H$_2$O could reach up to 60 kg H$_2$ m^{-3} [90,91]. Unlike NaBH$_4$ and LiBH$_4$, KBH$_4$ reacted very slowly with water to release 4 moles of hydrogen per mole of KBH$_4$ at room temperature [92]. It is considered that KBH$_4$ is not a suitable hydrogen storage material due to its low gravimetric hydrogen density, slow kinetics and high cost in production compared with NaBH$_4$.

7. Challenges and recommendations

It has been shown that hydrogen generation system through BH$_4{}^-$ hydrolysis is a good candidate to power PEMFC [82–89,93]. However, there are many engineering problems to be solved such as catalyst durability, mist elimination, crystallization of borates, thermal management, NaBH$_4$ production cost, and so on.

7.1. Catalyst durability

It is known that agglomeration of catalyst particles, surface oxidation of catalyst and catalyst component dissolution in alkaline NaBH$_4$ solutions are common reasons for catalysis deterioration of a catalyst. In practical uses, support failure of the catalyst support usually is a main reason to the catalyst deterioration. It is noted that hydrogen gas is generated in liquid solutions. Hydrogen bubbles would expanse their volumes in very high speed during hydrogen evolution. The higher the hydrogen generation rate, the higher the volume expansion rate of hydrogen bubbles. Then, a powerful shock on catalyst support would occur when a high hydrogen generation rate is required. Though use of porous materials as the support material [78–81] can effectively decrease the damage from this kind shock, how to avoid catalyst erosion caused by the flushing of the NaBH$_4$ solution is another key point to improve catalyst durability.

7.2. Mist elimination

In principle, hydrogen generated from borohydride hydrolysis should be pure as hydrogen is the only gas product. However, when hydrogen is generated from a borohydride solution, some mist of the solution would bring out with the generated hydrogen. The mist contains solution components such as NaBO$_2$, NaBH$_4$, NaOH and H$_2$O. It is not easy to be eliminated completely through a simple gas–liquid separation especially when hydrogen is produced at high rates and at high temperatures. It is afraid that these alkaline impurities in hydrogen would accumulate in the anode side of the PEMFC and result in performance degradation because the PEMFC works in an acidic medium. However, very few attentions on the mist elimination have been paid. It is considered that mist elimination is one of the most critical problems in development of hydrogen generation technology from NaBH$_4$ hydrolysis.

7.3. Crystallization of borates

Crystallization of borates after hydrogen generation limits the use of high concentrated NaBH$_4$ solutions for hydrogen generation because borate crystallization would consume H$_2$O to form hydrated borates. Precipitation of hydrated borates on catalysts and in pipelines of the system would result in decrease of hydrogen generation rate especially when using heterogeneous catalysts. Sometimes, it would damage the structure of catalyst support and block the hydrogen flow in the pipelines. Use of homogeneous catalysts can avoid the catalyst damage, but how to control the hydrolysis reaction is still a problem to be solved.

For a power generation system based on PEMFC using hydrogen as the fuel from NaBH$_4$ hydrolysis, use of water from the PEMFC may be one of the solutions to increase the system energy density though the water management in the PEMFC is also a big challenge.

7.4. Thermal management

BH$_4^-$ hydrolysis is an exothermic reaction. It is important to control the reaction temperature in the hydrogen generation system because the mist emission and borate crystallization are deeply influenced by the reaction temperature. Lower reaction temperature is favorable to depression of mist emission, but results in lower H$_2$O utilization due to the formation of NaB(OH)$_4$·2H$_2$O. Higher reaction temperature can improve the H$_2$O utilization but aggravate the mist emission. Therefore, the thermal management is a very important technology in the hydrogen generation system.

7.5. NaBH$_4$ production cost

Hydrogen from borohydride hydrolysis can be supply to the PEMFC on demand to power mobile electronic devices such as mobile phones, laptop computers, and so on. The integrated system of the hydrogen generator and the fuel cell is also a potential candidate to drive a vehicle such as car and boat. It is especially suitable to marine vehicles because half of hydrogen can be obtained from water conveniently. However, current production cost of NaBH$_4$ is too high to be used as a hydrogen carrier in civil applications. It is considered that meta-borate recycle is a key point to lower NaBH$_4$ production cost. Even though several fundamental researches on NaBH$_4$ synthesis technologies have been reported such as ball-milling synthesis [94–96] and thermal synthesis [97–104], more efforts should be paid to the development of new NaBH$_4$ synthesis processes.

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