Review

A comparison of sodium borohydride as a fuel for proton exchange membrane fuel cells and for direct borohydride fuel cells

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Abstract

Two types of fuel cell systems using $NaBH_4$ aqueous solution as a fuel are possible: the hydrogen/air proton exchange membrane fuel cell (PEMFC) which uses onsite H_2 generated via the $NaBH_4$ hydrolysis reaction (B-PEMFC) at the anode and the direct borohydride fuel cell (DBFC) system which directly uses $NaBH_4$ aqueous solution at the anode and air at the cathode. Recently, research on these two types of fuel cells has begun to attract interest due to the various benefits of this liquid fuel for fuel cell systems for portable applications.

It might therefore be relevant at this stage to evaluate the relative competitiveness of the two fuel cells. Considering their current technologies and the high price of $NaBH_4$, this paper evaluated and analyzed the factors influencing the relative favorability of each type of fuel cell.

Their relative competitiveness was strongly dependent on the extent of the $NaBH_4$ crossover. When considering the crossover in DBFC systems, the total costs of the B-PEMFC system were the most competitive among the fuel cell systems. On the other hand, if the crossover problem were to be completely overcome, the total cost of the DBFC system generating six electrons (6e-DBFC) would be very similar to that of the B-PEMFC system. The DBFC system generating eight electrons (8e-DBFC) became even more competitive if the problem of crossover can be overcome. However, in this case, the volume of $NaBH_4$ aqueous solution consumed by the DBFC was larger than that consumed by the B-PEMFC.
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Keywords: Sodium borohydride; Hydrolysis reaction; Proton exchange membrane fuel cells; Direct sodium borohydride fuel cells; Hydrogen

Contents

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) operating at room temperature require pure gaseous H_2 as a fuel. Therefore, a system capable of providing a stable and economical supply of pure H_2 gas (i.e. high purity H_2 generation, stable storage with a safe fuel phase) is a prerequisite before any other challenges in the use of PEMFCs can be addressed. Compressed H_2 or H_2 generated by the traditional methods, such as steam reforming of hydrocarbons or coal gasification, is believed to be a feasible solution for vehicle applications (>50 kW), but is not suitable for portable devices (<100 W) on account of the lower volumetric energy density of these hydrogen sources and the absence of sufficient storage space in small portable devices. Moreover, bulky hydrogen sources are generally not truly portable.

Therefore, the use of liquid fuel is believed to be the best solution for portable applications and this has led to the advent of direct methanol fuel cells (DMFCs). While DMFCs are considered as promising candidates for portable and mobile applications, their low performance and the problem of methanol crossover represent substantial hurdles which need to be overcome before their commercial success can be considered.

In recent years, sodium borohydride ($NaBH_4$) aqueous solution has become an interesting alternative as a liquid fuel for fuel cells [1–16] due to its many advantageous features such as high energy capacity and safety. However, despite their advantageous features, fuel cell systems using $NaBH_4$ aqueous solution as the fuel have to overcome one decisive hurdle to compete with the other fuel cell systems; the high price of $NaBH_4$.

In fact, the pure price of H_2 generated from $NaBH_4$ is about US$ 260 kg^{-1} (H_2). This is about 130 times higher than that of H_2 generated via the reforming of natural gas, about US$ 2 kg^{-1} (H_2) and even 50 times higher than H_2 produced by electrolysis using the electricity obtained from wind energy, about US$ 5 kg^{-1} (H_2) [17].

Therefore, the current high price of $NaBH_4$ (US$ 55 kg^{-1}) presents a serious restriction to the development of borohydride as an economically viable method of H_2 storage and/or generation.

However, one group of researchers [18] claims that the price of $NaBH_4$ could be reduced to US$ 1 kg^{-1} within the next 5 years and if it could be reduced further to US$ 0.55 kg^{-1}, this fuel cell system would become a major contender for various applications of fuel cells. The required cost reduction may be achievable via the new processes of $NaBH_4$ synthesis, mass production and the recycling of the reaction product, $NaBO_2$ [19–22]. According to these studies, $NaBH_4$ was synthesized by reacting $NaBO_2$ with MgH_2 or Mg_2Si by annealing the mixture of these two compounds under high H_2 pressure [20] and also in another study it was conveniently synthesized by the reaction of MgH_2 with $Na_2B_4O_7$ through ball milling at room temperature [21].

There are two types of fuel cell systems using $NaBH_4$ aqueous solution as the fuel: the PEMFC system which uses on-site H_2 generated via the $NaBH_4$ hydrolysis reaction in the hydrolysis reactor directly connected with the PEMFC (B-PEMFC), and

the direct borohydride fuel cell (DBFCs) system which directly uses $NaBH_4$ aqueous solution as an anodic fuel.

While the fuel for these two systems is the same $NaBH_4$ aqueous solution, they have one major, yet intriguing, difference. In B-PEMFC, it is necessary to generate as much H_2 as possible, whereas in the DBFC system, the production of H_2 must be suppressed as much as possible for adequate cell performance. Each system naturally has own advantages and drawbacks.

Much research on the $NaBH_4$ hydrolysis reaction for H_2 supply has been conducted over the decades. However, the performance of B-PEMFC based on experimental results has not been well reported and the studies in this area have not reported detailed results [2–4,8,9]. In fact, the current state of B-PEMFC development remains at the evaluation stage of whether this system is technologically feasible. The DBFC technology for commercial purposes is also only at the initial development stage.

This paper introduces and discusses some cases of the latest research on the two types of fuel cell technology: B-PEMFC and DBFC. Next, various factors, such as the amount of consumed $NaBH_4$ and fuel cell volume, are evaluated and the total cost of each system is analyzed to determine which type of fuel cell is more favorable. In addition, the relative prospects and competitive force of the two types are specifically described by comparing the factors exhibited when the systems are applied to a portable application at a power range of 20 W. Therefore, this paper is expected to provide useful and helpful information for the development of fuel cell technology using $NaBH_4$ aqueous solution as the fuel.

2. Sodium borohydride as a fuel for fuel cells

2.1. Sodium borohydride

In the late 1930s and early 1940s, workers at the University of Chicago produced a number of new borohydride compounds. Having obtained these new volatile compounds, they were requested to investigate further such compounds in support of the war effort. As a result, uranium borohydride [23,24] was successfully synthesized as a potential alternative to uranium hexafluoride. The U.S. Army Signal Corps became interested in $NaBH_4$ [23,25] as a potential source of field generated H_2 for signal balloons, and various researchers investigated it as a potential propellant for rocket engines [8,26]. Nowadays, $NaBH_4$ is primarily used as a reductant in the synthesis of organic chemical compounds and as a bleaching agent in the manufacture of paper [8]. $NaBH_4$ solution is traditionally used as a heat exchange medium in cooling applications.

The properties of $NaBH_4$ have been investigated by a number of researchers [8]. Davis et al. [27] determined the heat of formation by first determining the specific heat, density, and heat of reaction when $NaBH_4$ was reacted with excess dilute hydrochloric acid. Johnston and Hallett [28] measured the heat capacity of $NaBH_4$, and calculated the entropy and enthalpy from 15 to 300 K. Stockmayer et al. [29] determined the standard free energy of formation for the aqueous borohydride ion, as well
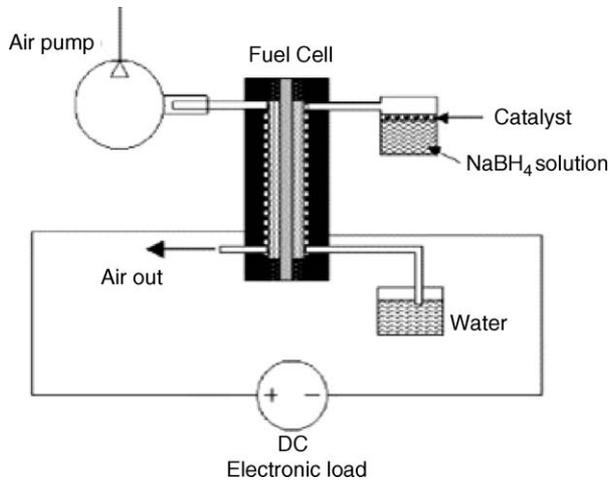
Fig. 1. Schematic diagram of B-PEMFC systems (in the single fuel cell, grey represents the electrolyte, dots the electrode, black with white dots the gasket and black the flow channel plate) [6].

as an estimate for the standard entropy of the ion. The heat of solution of NaBH$_4$ was measured and the heat of formation and the entropy derived by Gunn and Green [30].

2.2. B-PEMFC systems

The idea of this system is that the PEMFC utilizes the on-site H$_2$ generated via the NaBH$_4$ hydrolysis reaction as shown in Fig. 1.

In the system, first of all, NaBH$_4$ reacts rapidly with water to generate H$_2$ according to the hydrolysis reaction, as shown in Eq. (1):

$$NaBH_4(aq) + 2H_2O \rightarrow 4H_2 + NaBO_2(aq) + Heat(217\,kJ) \quad (1)$$

This reaction has been studied in detail for several decades [1–4,26,31–36] and is known to run via zero order kinetics [2]. As indicated by the stoichiometry in Eq. (1), half of the H$_2$ produced in the hydrolysis reaction is derived from the solution water, which accounts for the large amount of H$_2$ generated in this reaction. The advantageous features of this reaction (1) as a source of H$_2$ are listed in Table 1.

NaBH$_4$ solutions rendered basic with NaOH become chemically stabilized and do not generate significant amounts of H$_2$ under ambient conditions [3,36]. However, upon the addition of some heterogeneous catalysts, the hydrolysis rate of NaBH$_4$ can be accelerated dramatically. Many conventional catalysts have been proposed for the reaction [2–9,26,31,35,37,38], of which Ru-based catalysts are known to be the most effective for promoting H$_2$ generation [2,6].

The H$_2$ generated is then used as the gaseous fuel for the PEMFC coupled with the hydrolysis reactor to generate the electricity via Eqs. (2)–(4):
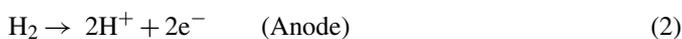
$$H_2 \rightarrow 2H^+ + 2e^- \qquad (Anode) \qquad (2)$$

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad (Cathode) \qquad (3)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad (Overall) \qquad (4)$$

Table 1
Advantageous features of NaBH$_4$ hydrolysis reaction as the H$_2$ supplier and storage

As the source of H$_2$	Advantageous features
Generation	Only occurs in the presence of selected catalysts and reaction rates are easily controlled by the catalysts
	Carried out even at 0 °C
	Sufficiently high purity of H$_2$
Storage and safety	Theoretical H$_2$ content of NaBH$_4$ solutions is 10.9 wt.%
	Volumetric and gravimetric H$_2$ storage efficiencies are high
	NaBH$_4$ solutions are stable in air for months and nonflammable
Reaction products	The reaction products including NaBO$_2$ are environmentally safe and can be recycled back to NaBH$_4$ using coke or methane
	The other product in the gas stream is water vapor

The additional benefits obtained in the B-PEMFC system are listed in Table 2. The disadvantages of this system are described in Section 4 of the present paper.

The development of the B-PEMFC system can be divided into two steps. The first is the development of a hydrolysis mechanism of NaBH$_4$ with a high reaction conversion and a H$_2$ generation rate sufficient to provide fuel for PEMFC. The second is the establishment of an effective system design for connecting this H$_2$ supply to a PEMFC system.

The former step is generally accepted as being the key issue. While much research has already been conducted into the generation of H$_2$ via the hydrolysis of NaBH$_4$, it is still questionable as to whether the amount of H$_2$ generated and the reaction rate are sufficient to provide the fuel for a PEMFC system. Recently, however, these technological issues have been overcome, both theoretically and experimentally, by the development of various catalyst systems. As a result, the reaction conversion rate has been increased to almost 100% at room temperature and the H$_2$ generation rate has been raised to a level sufficient for PEMFC. Subsequently, the B-PEMFC system has been applied and evaluated by many researchers. Table 3 summarizes the body of research which has been conducted since 2000.

As listed in Table 3, many catalyst systems such as Ru/anion exchange resin, Pt/LiCoO$_2$, Pt/carbon, Co powder/Ni foam, PtRu/LiCoO$_2$, and Co–B have been proposed and additional research has been conducted to optimize their composition.

Table 2
Advantageous features of B-PEMFC systems

On-site generation of H$_2$

Pure Pt can be used as the anode electrocatalyst of PEMFC

PEMFC system can be simplified due to the lack of need for an additional processor for cleanup

H$_2$ pressure/flow rates can be accurately controlled and made self-regulating by numerous feedback mechanisms

NaBH$_4$ can be quickly refueled simply by filling the reservoir with fresh NaBH$_4$ solution

Water vapor which is present can be used to humidify the PEMFC membrane

Water generated by the PEMFC can be returned to the NaBH$_4$ solution, allowing additional H$_2$ to be generated

Table 3
Various studies since 2000 on B-PEMFC using H_2 generated via $NaBH_4$ hydrolysis reaction

Reference	Used catalyst/support system in $NaBH_4$ hydrolysis reaction (used amount of catalysts; mg)	Compositions of $NaBH_4$ aqueous solution; wt.% (used solution volume; ml)	Average H_2 generation rate at 25 °C; H_2 l min^{-1} g^{-1}(catalyst) (overall conversion)	Estimated power level in B-PEMFC, kW g^{-1} (catalyst)	Comments
[2]	Ru (5 wt.%)/IRA 400 (anion exchange resin) (250)	20% $NaBH_4$, 10% NaOH (30)	0.2	~0.3 at.	$NaBO_2$ precipitation was dependent on the feed solution concentration
[3]	Pt (1.5 wt.%)/$LiCoO_2$ (256)	20% $NaBH_4$, 10% NaOH (27.5)[a]	2.8 at 22 °C (about 100%)	0.1–0.34	Pt–$LiCoO_2$ catalyst led to the enhancement of the hydrolysis reaction rate
[4]	Pt (20 wt.%)/C (acetylene black) (100)	10% $NaBH_4$, 5% NaOH (200 ml at a rate of 10 ml min^{-1})	2.3 (0.1 g^{-1} catalysts) (about 100%)	0.3 (0.1 g^{-1} catalysts)	Micro-pore structure of the catalysts played important roles in determining the hydrolysis reaction rate
[5]	Filamentary Ni mixed Co powder; Co powder/Ni foam	10% $NaBH_4$, 0.01 M KOH	0.096 (maximum) at 30 °C	–	Confirmed the purity of H_2 to be more than 99.99%
[6]	Ru (5 wt.%)/ion-exchange resin beads (20)	20% $NaBH_4$, 10% NaOH (9.17)[a]	0.09 (98.9%)	–	H_2 generation curve could be divided into four stages
[7]	PtRu (10 wt.%)/$LiCoO_2$ (125)	5% $NaBH_4$, 5% NaOH (25)	1.36 (about 100%)	–	PtRu–$LiCoO_2$, is excellent at $NaBH_4$ concentrations of up to 15 wt.%
[8]	Ru (1 wt.%)/carbon (500)	20% $NaBH_4$, 1% NaOH (20 ml optimum; 2 ml min^{-1})	1.14 (about 100%)	0.2–1.3	Bench-top hybrid power system, consisting of $NaBH_4$-PEMFC and batteries, is suitable for portable applications
[9]	Co–B (50)	20% $NaBH_4$, 10% NaOH	1.2 at 30 °C	2 W	A passive air-breathing 2 W PEMFC stack was successfully operated and powered a cellular phone

[a] Specific gravity of the 20% $NaBH_4$–10% NaOH solution; 1.09 [12].

According to these reports, $NaBH_4$ hydrolysis at room temperature is best carried out with 5–25 wt.% of $NaBH_4$ aqueous solution as the reactant to which 1–10 wt.% NaOH solution is added to stabilize the solution. Under these conditions, researchers reported a reaction conversion of approximately 100% and an average H_2 generation rate ranging from 0.93 to 2.8 $H_2 \, l \, min^{-1} \, g^{-1}$ (catalyst) which produced a PEMFC performance equivalent to 0.1–0.3 kW g^{-1} (catalyst). Among these systems, the $Pt/LiCoO_2$ system reported by Kogima et al. [3] in 2002 exhibited the highest reaction rate. According to their paper, a $Pt–LiCoO_2$ catalyst prepared by the conventional impregnated method could generate sufficient H_2 for PEMFC operation, both in terms of the rate and amount. In their experiment, 50–256 mg of the $Pt–LiCoO_2$ catalyst was placed in a sealed flask, and then 30 g of base-stabilized 20% $NaBH_4$ solution (10% NaOH and 70% H_2O) was dropped onto the catalyst. The H_2 generated was collected and its volume was measured by the water trap method. The measured reaction rates are shown in Fig. 2.

The authors of this report claimed that the average reaction rate of H_2 generation was 2.8 $H_2 \, l \, min^{-1} \, g^{-1}$ (catalyst) and that the reaction conversion was 100% at 22 °C. Based on their experimental results, they also claimed that 230–780 g of catalyst are needed to power a 77.5 kW PEM fuel cell for a transportation application. Note that in this paper we have used these results reported by Kogima et al. as the B-PEMFC standard for our own analysis and comparison of the B-PEMFC and DBFC systems.

2.3. DBFC systems

The DBFC fuel cell system directly uses the $NaBH_4$ solution as the fuel filled in or continuously supplied to the anodic chamber, as shown in Fig. 3.

In the system, the electricity is produced via the following anode and cathode reactions, as shown in Eqs. (5) and (6). The overall reaction of the system is shown in Eq. (7):

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \quad \text{(anode)},$$

$$E° = -1.24 \text{ V vs. SHE} \tag{5}$$

Fig. 2. Volume of H_2 generated as a function of time by different catalysts in 20% $NaBH_4$, 10% NaOH, 70% H_2O solution at 22 °C [3].
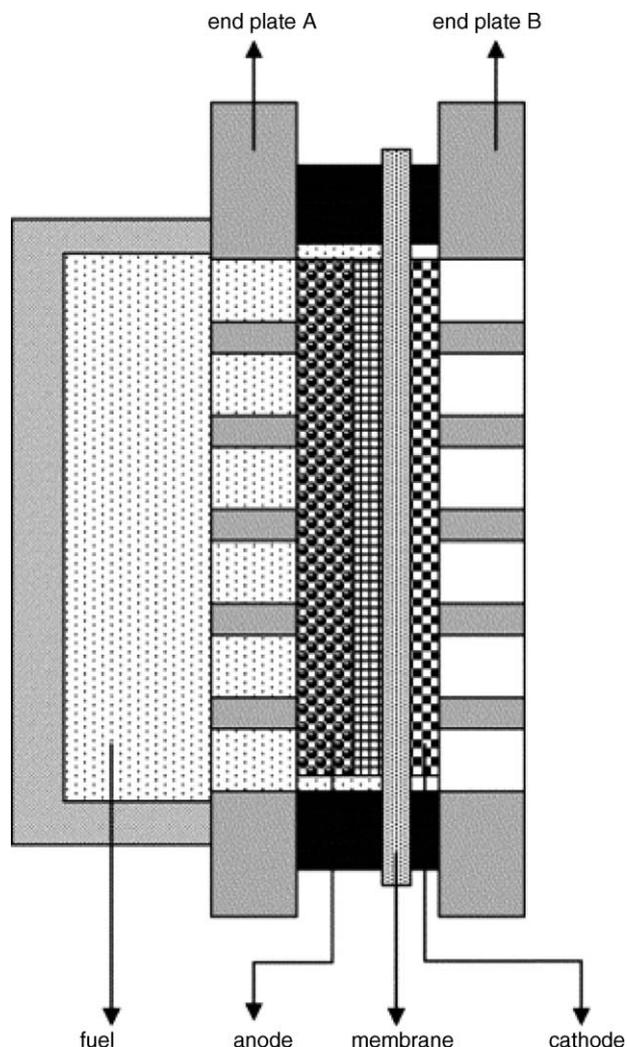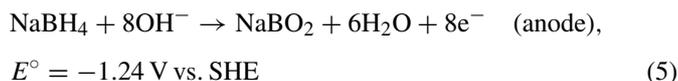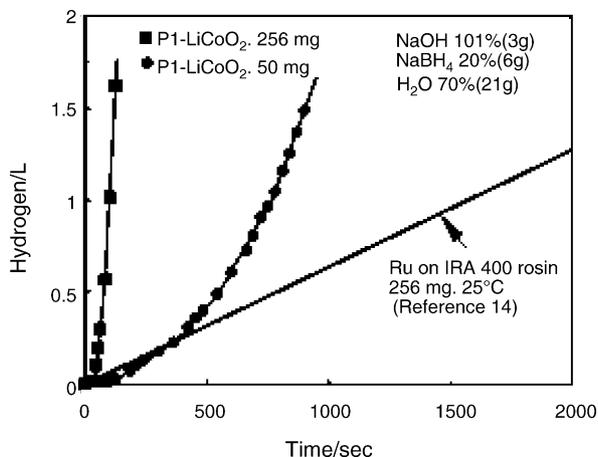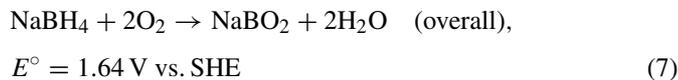
Fig. 3. Schematic illustration of DBFC (a top view) [14].

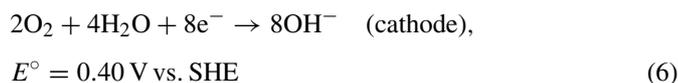$$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^- \quad \text{(cathode)},$$

$$E° = 0.40 \text{ V vs. SHE} \tag{6}$$

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O \quad \text{(overall)},$$

$$E° = 1.64 \text{ V vs. SHE} \tag{7}$$

DBFCs were first proposed in the early 1960s [39,40]. Indig and Snyder [39] reported that the direct electricity generation from borohydride ion could be practical [41]. Since then, research on DBFC technology stagnated until the late 1990s. Recently, however, vigorous research into DBFC has recommenced and raised expectations of the various benefits promised by this liquid fuel for fuel cell systems.

There are three types of DBFC according to the electrolyte applied [16]. When the KOH or anion exchange membrane (AEM) is employed as the electrolyte, the charge carrier and ion migration are the same as the OH^- ion which is transferred from the cathode to anode. On the other hand, in DBFC systems with an electrolyte of cation exchange membrane (CEM), Na^+
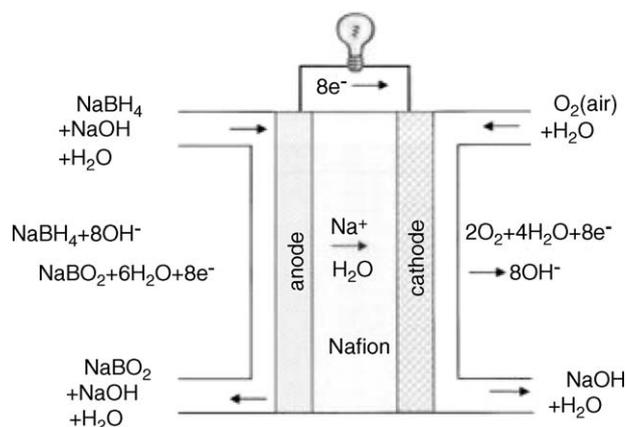
Fig. 4. Mechanism for electricity generation and mass transfer of DBFC using CEM [11].

migrates from the anode to cathode and carries the charges as shown in Fig. 4.

While each system has its own advantages and drawbacks, the CEM electrolyte results in the most efficient DBFC system in terms of the $NaBH_4$ crossover [16]. One of the most important factors in the realization of the DBFC as a viable fuel cell system is the inhibition of the $NaBH_4$ crossover. DBFC using AEM cannot solve this problem because $NaBH_4$ as an anion can easily permeate through an AEM. Therefore, the DBFC system described in this paper uses the CEM fuel cell system.

The most advantageous feature of DBFC is its highest theoretical energy density, $9.3\,Wh\,g^{-1}$ of $NaBH_4$, among the various fuel cell systems. However, the energy density substantially decreases in real cell operation. Theoretically, one ion of BH_4^- can generate eight electrons as shown in Eq. (5). However, in real systems, it is inevitable that the number of electrons actually utilized per ion of BH_4^- oxidized is less than eight. The most influential factor is the applied anode electrocatalyst system. It is reported that one ion of BH_4^- generates 6.9 electrons by using Au catalyst [10], 6 by using Pd catalyst [42] and 4 by using Ni catalyst [43]. However, the electron loss is not always determined by the electrocatalysts employed. The addition of a small amount of thiourea to NaOH (as the electrolyte) was effective in reducing the electron losses on Pt electrocatalysts [41].

The decrease of generated electrons leads to a decrease of the energy density to $7.6\,Wh\,g^{-1}$ at six electrons and $5.8\,Wh\,g^{-1}$ at four electrons. Furthermore, in DBFC, H_2 is evolved from the anode side, whether in an open-circuit condition or during operation. This H_2 gas which decreases the cell efficiency can be generated not only from the hydrolysis reaction (1) but also from the electrochemical reaction [39], as shown in Eq. (8):

$$NaBH_4(aq) + 4OH^- \rightarrow 2H_2 + NaBO_2(aq) + 2H_2O + 4e^-$$

(8)
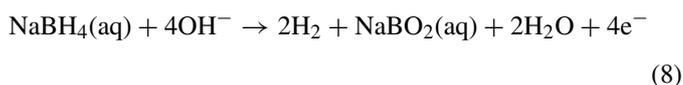
Therefore, the issues of how to restrain the H_2 evolution and how to obtain a complete eight-electron reaction are the key factors to improve the columbic efficiency of the DBFCs. In addition to high energy density and due to the advantageous

Table 4
Advantageous features of DBFC systems

High theoretical energy density, $9.3\,Wh\,g^{-1}$ of $NaBH_4$
Solution as fuel, no fuel modification or fuel processor
Cheap anode electrocatalysts are available (non-platinum catalysts is usable)
Anion exchange membrane electrolyte is usable
Cooling plates are not needed in fuel cell stack
Humidifier can be eliminated
Easy cell start up

features of the DBFC system summarized in Table 4, research on DBFC has recently been conducted.

In 1999, Amendola et al. [10] reported the performance of the DBFC system using Au–Pt alloy electroplated on carbon cloth as the anode while, the cathode was a commercial gas diffusion electrode separated from the anode by an AEM. Following further impressive research efforts over the next 5 years, the first demonstration of a DBFC system for laptop computer was presented in 2005 by the Materials and Energy Research Institute (MERIT), the inventor of the system [44]. In addition, according to the MERIT, they have succeeded in expanding the DBFCs from 10 to 400 W.

Table 5 summarizes the research on DBFC which has been conducted over the last 5 years.

As listed in Table 5, various studies on DBFC have been progressed using Au, Pt, Ni and Ni–Zr alloys as anode electrocatalysts with KOH, AEM and CEM electrolytes. These studies have increased the power density up to $290\,mW\,cm^2$ at $60\,°C$ and many conditions have been determined for increasing the efficient performance of the cell. No total efficiency data are given in these papers, especially as related to the loss of hydrogen resulting from hydrolysis and crossover in the DBFC. These losses are serious limitations in the case of the DBFC.

However, the best representative, state-of-the-art DBFC system [16] was constructed using a mixture of surface treated Zr–Ni Laves phase alloy such as $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ and Pd/C as the anode catalyst, carbon-supported Pt as the cathode catalyst and the Na^+ from Nafion membrane (NRE-211) as the electrolyte. According to the authors of the paper, a power density of $290\,mW\,cm^{-2}$ was achieved with this system at $60\,°C$. In addition, they claimed that a five-cell stack with an effective area of $67\,cm^2$ demonstrated a power output attaining $110\,W$ when the stack temperature reached $60\,°C$, even if the stack started at room temperature without air humidification. The performance of the single-cell stack is shown in Fig. 5.

The results of the report [16] were used in this paper as the basis for comparing the performance of the DBFC and B-PEMFC systems.

3. Analysis and discussion of the B-PEMFC and DBFC systems

3.1. Energy density and the amounts of $NaBH_4$ and feed solution consumed without crossover

When a feed rate of $4.73\,g\,(NaBH_4)\,s^{-1}$ of pure $NaBH_4$, corresponding to $1\,g$ of H_2 evolved per second in the $NaBH_4$

Table 5
Various studies since 1999 on DBFC

Reference	Anode catalysts, electrolytes, cathode	Compositions of NaBH₄ aqueous solution; wt.% (used solution volume; ml)	Cell performance	Comments
[10]	Au (97 wt.%)–Pt (3 wt.%)/C, anion conducting polymer membrane, –	5% NaBH₄, 25% NaOH	Specific energies; >3.6 Wh g^{-1} (NaBH₄), power densities; 20 (at 25 °C) ∼60 (at 70 °C) mW cm^{-2}	The number of electrons utilized per molecule of BH₄$^-$ oxidized was 6.9
[11]	$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ (2 mg cm^{-2}), Nafion 117, Pt (2 mg cm^{-2})/C	10% NaBH₄, 20% NaOH (300 at a rate of 200 ml min^{-1})	OCV; 1.2 V, power density; 190 mW cm^{-2} at 1.5 V at 85 °C	It was confirmed that cations (Na$^+$) were the charge carrier in DBFC
[12]	$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ (2 mg cm^{-2}), Nafion 117, Pt (1 mg cm^{-2})/C	10% NaBH₄, 20% NaOH (100 at a rate of 500 ml min^{-1})	Power density; 60 mW cm^{-2} at 1.0 V at 60 °C	Cell polarization was increased according to the concentration of NaOH which decreased the mobility of the charge carrier (Na$^+$)
[13]	Pt (60 wt.%)/C, 6 M KOH solution electrolyte, Pt (60 wt.%)/C	0.5 M NaBH₄, 1 M KOH	Specific energies; 6.57 Wh g^{-1} (NaBH₄) at 25 °C	Anode microstructure acts as a channel to the liquid fuel
[14]	Ni powder (167 mg cm^{-2}), Nafion NRE211, Pt (1 mg cm^{-2})/C	5% NaBH₄, 6 M NaOH (30 ml)	Power density; 40 mW cm^{-2} at 25 °C	Membrane properties were found to be a decisive factor for cell performance
[15]	Au gauge, cation conducting polymer membrane, Pt (0.6 mg cm^{-2})/C	25% NaBH₄, 6 M NaOH	Power density; 140 mW cm^{-2} at 1 V	To negate the need for sodium and to obtain the best performance, it is believed an anion exchange membrane is needed
[16]	$Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ and Pd/C, Nafion NRE211, Pt/C	10% NaBH₄, 20% NaOH (150 ml min^{-1})	Power density; 290 mW cm^{-2} at 60 °C	NaBH₄ utilization depends on the applied anode catalysts, NaBH₄ concentration and operation temperature

Table 6
Theoretical and operational power generated and energy density of each fuel cell system: basis; a feed rate of 4.73 g (NaBH₄) s^{-1} (0.13 mol s^{-1}) as the fuel (without considering the crossover in the DBFC)

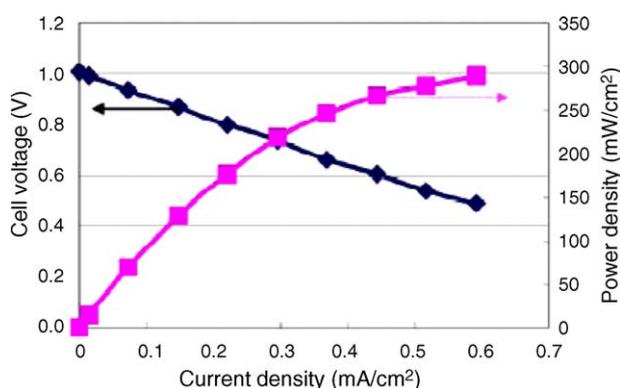| Fuel cell systems	Theoretical power; kW (theoretical electromotive force; V)	Theoretical energy density; Wh g^{-1} (NaBH₄)	Operational power; kW (operational voltage; V)	Operational energy density; Wh g^{-1} (NaBH₄)	Feeding rate of NaBH₄ needed for generating 1 W; mg min^{-1} (NaBH₄)
B-PEMFC	118.70 (1.23)	6.97	67.55 (0.7)	3.97	4.20
8e-DBFC	158.26 (1.64)	9.30	96.50 (1.0)	5.67	2.94
6e-DBFC	128.83 (1.78)	7.57	72.38 (1.0)	4.25	3.92
4e-DBFC	98.91 (2.05)	5.81	48.25 (1.0)	2.83	5.88

Fig. 5. Single-cell performance of DBFC [16].

hydrolysis reaction with 100% conversion, was used as the fuel for the B-PEMFC and for the three types of DBFC generating eight, six, and four electrons, respectively, the calculated theoretical and operational power and energy density of each fuel cell system are listed in Table 6.

Table 6 also shows the comparative energy efficiency of each fuel cell system at this condition. The theoretical energy density of the B-PEMFC was calculated to be 6.97 Wh g^{-1} (NaBH₄) at 1.23 V, which was similar to the value of 7.57 Wh g^{-1} (NaBH₄) at 1.78 V of the six electron generating DBFC (6e-DBFC) [16]. When the B-PEMFC was operated at 0.7 V, its operating energy density was calculated to be 3.97 Wh g^{-1} (NaBH₄), which was 70% of that of the 8e-DBFC and 95% of that of the 6e-DBFC. On the basis of the operating results, the feeding rate of NaBH₄ needed to generate 1 W was calculated to be 4.20 mg min^{-1},
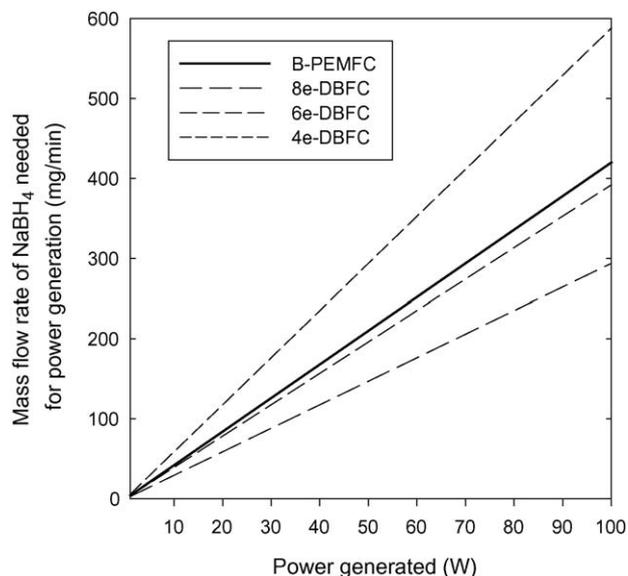
Fig. 6. Mass flow rates of NaBH$_4$ consumed at various power generations in each fuel cell system (without considering the crossover in the DBFC).

Fig. 7. Volume flow rates of NaBH$_4$–NaOH aqueous solution consumed at various power generations in each fuel cell system (without considering the crossover in the DBFC).

which was 43% and 5% more than those of the 8e-DBFC and 6e-DBFC systems without crossover, respectively.

The amount of NaBH$_4$ consumed by each cell is the key factor to consider when comparing their efficiencies. For example, when each cell was operated at 1 W for 1 h, the cost of NaBH$_4$ was US$ 0.01386 in B-PEMFC, compared to US$ 0.0097 in 8e-DBFC and US$ 0.01294 in 6e-DBFC. Therefore, the difference in the absolute amount (and its cost) of consumed NaBH$_4$ between B-PEMFC and 8e-DBFC increased with increasing amount of power generated, as shown in Fig. 6. This difference also severely widened according to the operating time.

However, these results were calculated solely based on the theoretical energy densities of the two cells, without considering the additional loss of NaBH$_4$ solution due to the crossover in the DBFC system. These effects will be described in a later Section 3.3 in present paper.

On the other hand, the amount of NaBH$_4$–NaOH aqueous solution used as the fuel in each cell, which is related to the fuel cell volume, varied. Considering the optimum compositions of the NaBH$_4$–NaOH aqueous feeding solution, i.e. 20% NaBH$_4$–10% NaOH for B-PEMFC and 10% NaBH$_4$–20% NaOH for DBFC, the volume of NaBH$_4$ aqueous solution consumed by B-PEMFC for the generation of 1 W was calculated to be 19.28 ml min^{-1}, which was 78 and 58 vol.% of the 8e-DBFC and 6e-DBFC values, respectively. These calculations were based on the specific gravities of 1.09 for 20% NaBH$_4$ and 1.19 for 20% NaBH$_4$ solution [12]. Fig. 7 shows the volume of solution needed as a function of the generating power for each fuel cell system. In this figure, the volume of feeding solution required by DBFC increases more rapidly than that required by B-PEMFC with increasing power generation. Furthermore, if the crossover in the DBFC is taken into consideration, the difference in the feeding solution volume between the two types of fuel cells could be severely widened.
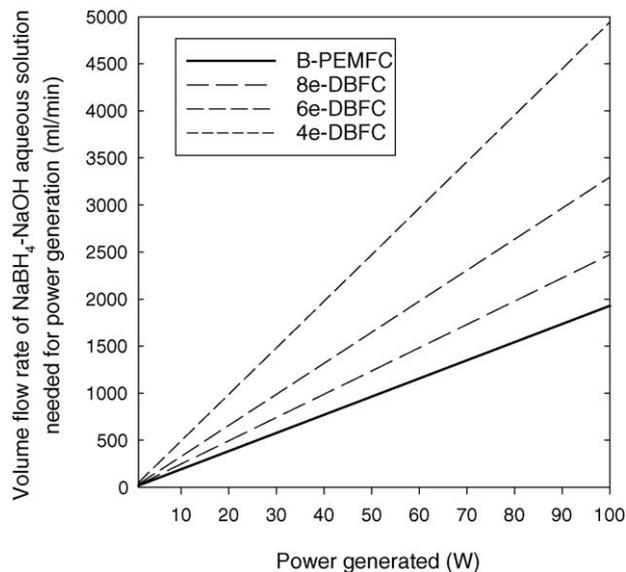
3.2. Comparison between B-PEMFC and DBFC without crossover in 20 W portable application

3.2.1. Rate of consumption of NaBH$_4$ and its aqueous feeding solution

When each fuel cell system was applied to a portable electronic device, namely a 20 W-laptop computer, the NaBH$_4$ feed rates are listed in Table 7.

These values were also calculated solely based on their theoretical energy densities, without considering the crossover in the DBFC system.

The consumptions of NaBH$_4$ were 84, 59 and 78.4 mg min^{-1} in the B-PEMFC, 8e-DBFC and 6e-DBFC systems, respectively. This means that B-PEMFC costs US$ 0.083 and 0.018 h^{-1} more to operate in terms of the fuel costs than the 8e-DBFC and 6e-DBFC systems, respectively, when the 20 W laptop computer is used.

In each fuel cell, the volumes of NaBH$_4$–NaOH aqueous solution are also listed in Table 7. In B-PEMFC, 385.5 ml min^{-1} of NaBH$_4$ aqueous solution was needed. At the same time, based on the results reported in the literature by Kogima et al. [3], 71 mg of Pt–LiCoO$_2$ catalyst is needed for the NaBH$_4$ hydrolysis reaction. However, in 8e-DBFC, 494.1 ml min^{-1} of 10% NaBH$_4$ aqueous solution was needed. Therefore, the auxiliary reactor including catalysts for the NaBH$_4$ hydrolysis reaction, with a volume of 385.5 ml, is separately equipped out of the fuel cell in B-PEMFC. On the other hand, the space to accommodate 491.1 ml within the fuel cell is required in 8e-DBFC systems.

3.2.2. Size of the fuel cell systems based on their state-of-the-art fuel cells

The typical performance of a single cell PEMFC is a voltage of 0.6–0.7 V and a cell current density of 0.3–0.6 A cm^{-2}, which equates to a power density of 200 mW cm^{-2} or more. Recently, however, a power density of more than 720 mW cm^{-2} at 0.6 V

Table 7
Comparison of feed rate between B-PEMFC and DBFC in portable application with a power output of 20 W (without considering the crossover in the DBFC)

Fuel cell systems	Feed rate of $NaBH_4$; mg min^{-1} (operational voltage; V)	Feed rate of NaOH; mg min^{-1}	Feed rate of water; mg min^{-1}	Feed rate of $NaBH_4$–NaOH aqueous solution; mg min^{-1}	Feed rate of $NaBH_4$–NaOH aqueous solution; ml min^{-1}
B-PEMFC[a]	84.0 (0.7)	42.0	294.0	420.0[a]	385.5
8e-DBFC[b]	58.8 (1.0)	117.6	411.6	588.0[b]	494.1
6e-DBFC[b]	78.4 (1.0)	156.8	548.8	784.0[b]	658.9
4e-DBFC[b]	117.6 (1.0)	235.2	823.2[b]	1176.0[b]	988.3

[a] 20% $NaBH_4$–10% NaOH solution, S.G. = 1.09 [12].
[b] 10% $NaBH_4$–20% NaOH solution, S.G. = 1.19 [12].

has been reported [45]. According to other papers [46,47] concerning UTC Fuel Cells, a power density of 680 mW cm^{-2} was obtained at ambient pressure and 65 °C. In addition, in 2005, Manthiram et al. [48] reported that the best performance was achieved at a Pt loading of 0.1 mg cm^{-2} with a maximum power density of 714 mW cm^{-2} using 20 wt.% Pt/C and a Nafion 115 membrane. Therefore, even though the lowest power density of a PEMFC was assumed to be 500 mW cm^{-2}, the area of the B-PEMFC required for the production of 20 W was calculated to be 10 cm^2. On the other hand, Li et al. [16] reported that the maximum power density of the DBFC (this may be the state-of-the-art) was 290 mW cm^{-2} and that a single cell area of 68 cm^2 was needed for 20 W power generation.

3.3. Cost of the fuel cell systems considering crossover in DBFC

The cost of a typical PEMFC comprises the costs of the membranes, platinum, electrodes, bipolar plates, peripherals and the assembly process, of which the bipolar plate and the electrode including platinum constitute approximately 80% of the total cost. While the total cost of a PEMFC varies according to the application field, the currently accepted value is approximately US$ 0.6 W^{-1} [49]. Assuming that the additional cost for a B-PEMFC system, such as the reactor used for the $NaBH_4$ hydrolysis reaction and its system of connection to the PEMFC, totaled a maximum of US$ 0.6 W^{-1}, the total cost of the B-PEMFC is about US$ 1.2 W^{-1}. Therefore, the total cost of the B-PEMFC was calculated to be US$ 24 for 20 W power generation.

On the other hand, the researchers in MERIT [44] announced in 2005 that they planned to sell a 20 W DBFC for a laptop computer at a price of US$ 90 in 2006. However, considering that a common formula for the evaluation of the manufacturing cost is 1/3 of the selling cost, this implies that the fixed cost of the DBFC will be equal to US$ 1.5 W^{-1} or US$ 30 for 20 W power generation.

When the DBFC system with a power output of 20 W (a single cell area of 68 cm^2) is operated for up to 3000 h, additional loss of $NaBH_4$ solution is inevitable due to the crossover in the DBFC system, even in the case of a CEM-DBFC, which can minimize the $NaBH_4$ crossover. Therefore, in order to calculate the total cost of real DBFC systems, the additional cost of the $NaBH_4$ consumed should be considered. According to a previ-

ous paper [15], the additional loss of $NaBH_4$ due to crossover was calculated to be 4.01×10^{-7} mol cm^{-2} s^{-1} in the case of Nafion 117 electrolytes used. If so, an additional 3.71 g h^{-1} of $NaBH_4$ is needed for a DBFC with a power output of 20 W (a single cell area of 68 cm^2). This corresponds to US$ 0.2 h^{-1} which is almost the same amount of $NaBH_4$ solely reacted in DBFC systems.

Considering the crossover in DBFC systems, when a fuel cell with a power output of 20 W is operated for up to 3000 h, the total costs of each fuel cell system, including the fixed cost and the cost of $NaBH_4$ consumed, are shown in Fig. 8.

As shown in Fig. 8, the B-PEMFC system is the most competitive of the fuel cell systems. On the other hand, if the crossover problem were to be overcome in DBFC systems, the results would be different, as shown in Fig. 9.

In Fig. 9, the total cost of the 6e-DBFC system is very similar to that of the B-PEMFC system. However, in this case, the volume of $NaBH_4$ aqueous solution consumed by 6e-DBFC is 1.7-fold higher than that consumed by B-PEMFC. In addition, the 8e-DBFC system becomes even more competitive than the B-PEMFC system and its volume of $NaBH_4$ aqueous solution consumed is 1.3-fold higher than that consumed by B-PEMFC.
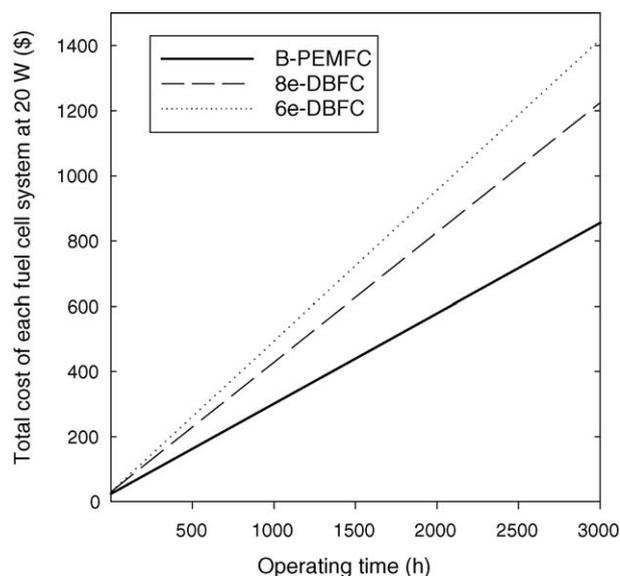

Fig. 8. Total cost of each cell system at 20 W output (considering the crossover; 4.01×10^{-7} (mol ($NaBH_4$) cm^{-2} s^{-1}) in Nafion 117 electrolytes used in the DBFC [15]) according to operating time.
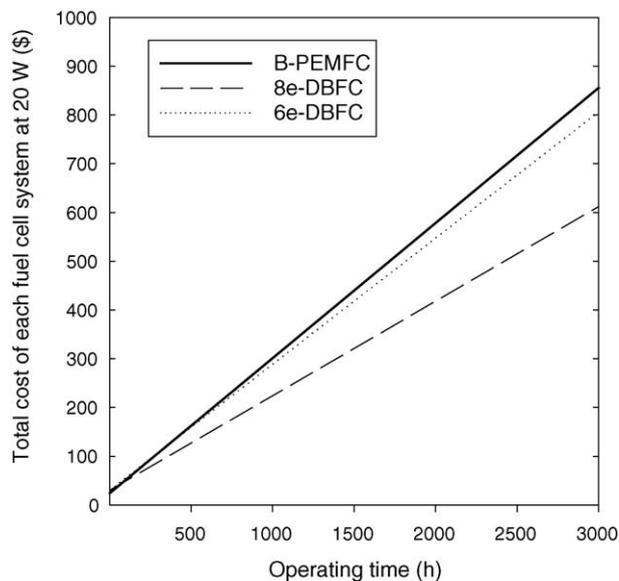
Fig. 9. Total cost of each cell system at 20 W output (without considering the crossover in the DBFC) according to operating time.

4. Remaining issues

4.1. B-PEMFC

While many recent studies have confirmed the technological availability of the B-PEMFC system, many challenges remain to be overcome before it can be put to practical use. These are listed in Table 8.

Among these challenges, as mentioned above, the key factor is the development of $NaBH_4$ hydrolysis catalysts which provide for full conversion and a sufficient H_2 generation rate.

Table 8
Remaining challenges of B-PEMFC systems

Steps for the development of B-PEMFC systems	Remaining challenges
Development of an economic hydrolysis reaction of $NaBH_4$ with a high conversion and an optimum reaction rate	Optimum catalyst selection and its amount
	Design of the hydrolysis reactor with the catalyst for on-site H_2 generation
	Development of catalyst tolerant to deactivation
	Treatment of the product not to block catalyst active sites
Establishment of an effective system design for connecting to a PEMFC	Optimum and compact design for connecting the hydrolysis reactor and PEMFC
	Simple refueling system of fresh $NaBH_4$ solution
	Water re-using system between hydrolysis reactor and PEMFC

Table 9
Remaining challenges of DBFC systems

Steps for the development of DBFC systems	Remaining challenges
Anode reaction	Development of anode electrocatalysts to generate eight electrons utilized per ion of BH_4^- and to inhibit the H_2 evolution
	Development of $NaBH_4$ aqueous solution to reduce the H_2 evolution
	Development of electrocatalysts tolerant to deactivation
	Volume reduction of $NaBH_4$ aqueous solution
Fuel cell systems	Development of MEA tolerant to crossover
	Up to $500\,mW\,cm^{-2}$ of operation power density is needed
	Treatment of NaOH accumulation at the cathode, and $NaBO_2$ accumulation at the anode
	Design of cell for simple fuel maintenance
	Adjustments in electrode and cell structure to inhibit the H_2 evolution

4.2. DBFC

The remaining challenges in the quest to develop practical DBFC systems are summarized in Table 9.

Among these challenges, as mentioned above, the key issue is the inhibition of the $NaBH_4$ crossover. The development of a membrane electrolyte assembly or liquid diffusion layer, which is more resistant to crossover, could be a solution to this problem. In addition, the enhancement of the power density of the DBFC should be achieved, which implies a decrease in the effective area of the cell for purpose of reducing the crossover.

The development of methods of obtaining eight-electron reactions and restraining the borohydride hydrolysis are also important for improving DBFC technologies. Using materials with a high H_2 over-potential and the use of surface treatment technology are considered to be the best way to meet these challenges. In addition, in portable applications the cell volume is very important, which requires a reduction in the volume of the $NaBH_4$ aqueous solution.

5. Conclusions

In this paper, we addressed the issue of which type of fuel cell is more competitive: the B-PEMFC or DBFC?

While there are a lot of factors involved in answering this question, their relative competitiveness was primarily dependent on the extent of $NaBH_4$ crossover in the DBFC systems. This analysis was entirely conducted based on current technologies and the current high price of $NaBH_4$. When taking into consideration the crossover in the DBFC systems, the total cost of the B-PEMFC system made it the more competitive of the two fuel cell systems. On the other hand, if the crossover problem in the DBFC systems were to be overcome, the total cost of the 6e-DBFC system would be very similar to that of the B-PEMFC system. However, in the analysis of this case, the

volume of NaBH$_4$ aqueous solution consumed by 6e-DBFC was 1.7-fold larger than that consumed by B-PEMFC. In addition, the 8e-DBFC system became even more competitive than the B-PEMFC system with slightly larger feeding solution volume.

Acknowledgement

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