

# Direct borohydride fuel cell: Main issues met by the membrane–electrodes-assembly and potential solutions

Umit B. Demirci\*

*Laboratoire des Matériaux Surfaces et Procédés pour la Catalyse (LMSPC), CNRS, UMR-7515,  
Université Louis Pasteur, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France*

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## Abstract

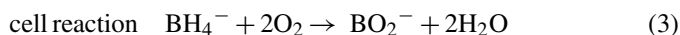
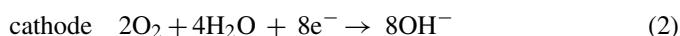
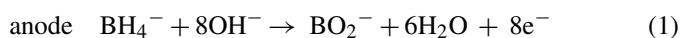
The direct borohydride fuel cell (DBFC) is a fuel cell for which there is consensus about its promising commercial future as a portable power system. However, its development faces three main issues: the borohydride hydrolysis (issue 1) and crossover (issue 2), and the cost (issue 3). These issues are encountered by the membrane–electrodes-assembly. By a discussion around these three issues, the present paper reviews the experimental aspects. The discussion stresses on the opportunities of improvements and reviews the potential solutions that are proposed in the open literature. For each issue, the best solution seems to be a combination of improvements. The issue 1 may be solved thanks to a gold-based anode catalyst and an optimized fuel. The solution to the issue 2 may be a more efficient membrane combined with an optimized fuel and an inactive-towards-borohydride cathode catalyst like  $\text{MnO}_2$ . Regarding the issue 3, cheaper materials and better fuel use efficiency are the keys. The DBFC is still in a development phase with a small number of years of R&D invested and it appears that there are real improvement opportunities on the path of the DBFC marketing.

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**Keywords:** Direct borohydride fuel cell; Review

## 1. Introduction

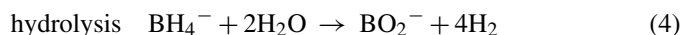
The direct borohydride fuel cell (DBFC) is a quite novel fuel cell that is based on the borohydride oxidation and the oxygen reduction:



with  $E^\circ_{\text{anode}} = -1.24$  V versus standard hydrogen electrode (SHE),  $E^\circ_{\text{cathode}} = -0.40$  V versus SHE and  $E^\circ_{\text{cell}} = -1.64$  V. The oxidation reaction takes place under an alkaline medium because the borohydride ions are not chemically stable in acidic media.

The DBFC can, thermodynamically and energetically, be compared to the direct methanol fuel cell (DMFC) and the polymer electrolyte membrane fuel cell (PEMFC). The comparison is favourable to the DBFC technology (Table 1). The DBFC theoretical electromotive force (1.64 V) is higher than those of the DMFC (1.21 V) and of the PEMFC (1.23 V). The theoretical conversion efficiencies of the DBFC and of the DMFC are similar (0.91 and 0.92, respectively) but are higher to that of the PEMFC (0.83). Finally, the direct oxidation of borohydride involves eight electrons per molecule versus two and six for hydrogen and methanol, respectively. Hence, the specific energy of the DBFC is 50% higher than that of the DMFC but does not reach 30% of the specific energy of the PEMFC fed with hydrogen.

For the DBFC, the ideal eight-electron oxidation (1) is not effective because hydrolysis of borohydride occurs in some extent:



This side reaction hinders the effective use of the  $\text{BH}_4^-$  faradic capacity since, for every molecule of hydrogen formed

\* Tel.: +33 388 24 27 51; fax: +33 388 24 27 68.

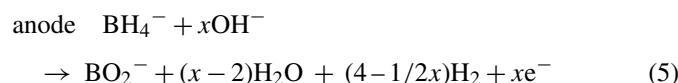
E-mail addresses: [umit.demirci@ecpm.u-strasbg.fr](mailto:umit.demirci@ecpm.u-strasbg.fr),  
[umitbilgedemirci@yahoo.fr](mailto:umitbilgedemirci@yahoo.fr).

Table 1  
Thermodynamic and energy characteristics of the DBFC, DMFC and PEMFC systems

	DBFC (Na <sup>+</sup> )BH <sub>4</sub> <sup>-</sup> /O <sub>2</sub>	DMFC CH <sub>3</sub> OH/O <sub>2</sub>	PEMFC H <sub>2</sub> /O <sub>2</sub>
Fuel molecular weight (g mol <sup>-1</sup> )	37.832	32.042	2.014
Electrons number <sup>a</sup>	8	6	2
Electromotive force (V)	1.64	1.21	1.23
Theoretical specific energy (Wh kg <sup>-1</sup> )	9295	6073	32707
Pure compound capacity (Ah kg <sup>-1</sup> )	5668	5019	26591
Conversion efficiency (%)	0.91	0.92	0.83

<sup>a</sup> Number of electrons involved during the direct oxidation.

two electrons are no longer available to provide electrical energy. It is one of the main disadvantages of the DBFC. The actual anodic reaction can be written as [1]:



The first investigations about the DBFC date back to the 1960s [2,3]. However, there has been a three-decade hiatus in the R&D of borohydride fuel cells, as Gyenge [4] justly wrote. Since few years, the investigations seem to intensify as it is well illustrated by three recent papers [5–7]. The Suda and co-workers' papers [5,8] show the high potential of the DBFC. Basing their discussion on the construction of a 100 W five-cell stack, the authors stress on its promising capacity. To resume Suda and co-worker [5], the DBFC is competitive with the PEMFC in the cell performance and, according to the PEMFC development history it is no doubt that the DBFC power density can reach up to 500 mW cm<sup>-2</sup> within several years. This optimistic view has very recently been reinforced by Miley et al. [9,10] who claimed their system reached a power density of 600 mW cm<sup>-2</sup>.

A first review, proposed by Lakeman and co-workers [6], stresses on the promising future of the DBFC and the issues to solve. A second review, proposed by Wee [7], compares two different borohydride-based fuel cells: the indirect borohydride fuel cell (IBFC) where borohydride is used as hydrogen generator and the DBFC. The DBFC technology faces some issues and mainly three: the borohydride hydrolysis, the borohydride crossover and the DBFC cost. This last issue is twice reviewed by Wee [7,11]. On the one hand, the author [7] compares the competitiveness of both DBFC and IBFC. On the other hand, the author [11] answers the following question: which type of fuel cell, between DMFCs and DBFCs, is more competitive for portable application? This analysis makes appearing that the DBFC is superior in terms of cell size and fuel, while its total cost for electricity generation is higher.

The present paper proposes a discussion about the experimental aspects of the DBFC that are the keys for solving the main issues the DBFC is facing, i.e. the borohydride hydrolysis, the borohydride crossover and the DBFC cost. As the cost issue was well reviewed by Wee [7,11] in two different papers, it will not be developed as lengthily as for the two other issues. This paper reviews the potential solutions that were suggested in the open literature to overcome these issues.

## 2. First main issue: borohydride hydrolysis

### 2.1. Anode electrocatalyst

The investigations about the DBFC electrocatalysts mainly deal with the anode ones. Lakeman and co-workers [6] and Wee [7] reviewed the different anode catalysts already tested: noble metals (Pd, Pt, Au), transition metals (Ni, Cu), AB<sub>5</sub>- and AB<sub>2</sub>-type hydrogen storage alloys. Suda [8] noticed that noble metals conveniently applied in the PEMFCs for converting H<sub>2</sub> to H<sup>+</sup> were not required in the DBFC.

The main objective is to find an anode catalyst inactive towards the borohydride hydrolysis. Gyenge and co-workers [12–14] proposed colloidal Os and Os-based alloys (Os–Sn, Os–Mn and Os–V), colloidal Au and Au-based alloys (Au–Pt, Au–Pd) and colloidal Pt and Pt-based alloys (Pt–Ni, Pt–Ir), the alloys metals being in 1:1 atomic ratio. Pt–Ir and Pt–Ni were the most active catalysts, giving a cell voltage of 0.53 V at 100 mA cm<sup>-2</sup> and 60 °C (for Au–Pt, the cell voltage was 0.47 V). Chatenet et al. [15] studied the Au and Ag catalysts, either bulk or nanodispersed over carbon. Gold showed better kinetics than silver. The nanodispersed metals showed better kinetics than the bulk metals. The authors concluded then that the carbon-supported gold nanoparticles were more promising materials for the DBFC.

Regarding the hydrogen storage alloys, Wang et al. [16,17] have worked on AB<sub>5</sub>-type LaNi<sub>4.5</sub>Al<sub>0.5</sub> alloy and Si-modified LmNi<sub>4.78</sub>Mn<sub>0.22</sub> alloy, which showed promising catalytic activities in both oxidation and hydrolysis of the fuel. A non-negligible interest of these materials was that the generated hydrogen was adsorbed and oxidized to produce electric energy; such behaviour was similar to that of the hydrogen storage alloy in nickel–metal hydride batteries [16]. In other words, in such fuel cell, the anode electrode is a place where borohydride oxidizes and where in parallel hydrogen generated from borohydride oxidizes as well, both contributing to the generation of electrons. However, Liu and Suda [18] suggested that there existed a competition between the two electrochemical oxidation reactions and that the electrochemical oxidation of atomic hydrogen was kinetically favourable only at low borohydride concentrations and low temperatures. The coulombic efficiency was only increased at low borohydride concentrations. The hydrogen storage alloys are promising materials as anode catalyst for the DBFCs, even if they also have high catalytic activity in the generation of hydrogen [16,17,19]. Wang and Xia [20] noticed that the hydrogen storage capacity of such alloys was limited. Unfor-

Table 2  
Laboratory-prepared metal-based electrocatalysts for the DBFCs anode

Catalyst	Support	Metal(s) content	Preparation method	Reference
Ag	Carbon <sup>a</sup>	60 wt. %	Impregnation	[25]
Au	Carbon <sup>a</sup>	60 wt. %	Impregnation	[24,25]
Au	Carbon <sup>b</sup>		Electrochemical deposition	[21]
Au	Carbon <sup>b</sup>		Electroless plating	[22]
Au	Titanate nanotubes <sup>c</sup>	10 wt. %	Ion exchange adsorption and chemical reduction	[23]
Au	Carbon <sup>a</sup>	20 wt. %	Modified Bönneinan	[13]
Au–Pt	Carbon <sup>b</sup>	97–3 wt. %	Electrochemical deposition	[21]
Au–Pt	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[13,14]
Au–Pd	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[13]
Ni	Carbon <sup>a</sup>	60 wt. %	Impregnation	[25]
Os	Carbon <sup>a</sup>	10, 20 and 30 wt. %	Modified Bönneinan	[12]
Os–Sn	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[12]
Os–Mo	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[12]
Os–V	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[12]
Pd	Carbon <sup>a</sup>	60 wt. %	Impregnation	[25]
Pt	Carbon <sup>a</sup>	20 wt. %	Modified Bönneinan	[14]
Pt	Carbon <sup>a</sup>	60 wt. %	Impregnation	[25]
Pt–Ni	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[14]
Pt–Ir	Carbon <sup>a</sup>	20 wt. %, 1:1 atomic ratio	Modified Bönneinan	[14]

<sup>a</sup> Vulcan XC-72.

<sup>b</sup> Carbon type not given.

<sup>c</sup> TiO<sub>2</sub> prepared by alkaline hydrothermal treatment.

tunately, one can regret that, among the published works, none directly compares the AB<sub>5</sub>-type alloys to e.g. Pt-based catalysts. Finally, their lower cost (compared to Pt) and their commercial availability are advantages.

The anode catalyst is either laboratory-prepared or purchased. The metal-based catalysts prepared at the laboratory [12–14,21–25] are listed in Table 2. The metal-based catalysts, purchased and used as received [1,4,15,23,26–33], are given in Table 3. The AB<sub>2</sub>- and AB<sub>5</sub>-type hydrogen storage alloys [16,17,19,20,34–38] are given in Table 4.

The catalyst preparation method is very important because the physical and chemical characteristics of the catalyst strongly depend on it, e.g. the synthesis of highly dispersed small metallic particles is sensitive towards the preparation method. For example, gold is a noble metal for which the high catalytic activity is unexpected as bulk gold is quite inert [39]. This behaviour changes, if gold is highly dispersed as nanosized particles on certain oxides [15]. The catalytic performance of Au is defined by three major factors: contact structure, support selection and particle size [40]. In such context, the nanomaterial-based catal-

Table 3  
Purchased metal-based electrocatalysts for the DBFCs anode

Electrocatalyst	Details	Reference
Ag	Disk electrode	[31]
Ag	Bulk and polycrystalline	[15]
Ag/C	10 wt. %, Vulcan XC-72 carbon supported	[30]
Ag/C	10 wt. %, nanodispersed over Vulcan XC-72 carbon	[15]
Au	Disk electrode, diameter 5 mm	[26]
Au	Disk electrode, diameter 1 mm	[4]
Au	Powder	[1]
Au	Foil (bulk)	[23]
Au	Bulk and polycrystalline	[15]
Au/C	10 wt. %, Vulcan XC-72 carbon supported	[23,30,33]
Au/C	10 wt. %, nanodispersed over Vulcan XC-72 carbon	[15]
Cu	Powder	[1]
Ni	Powder	[1,27,29]
Ni Raney	Powder	[1]
Pd/C	10 wt. %, Vulcan XC-72 carbon supported	[1,30]
Pt	Disk electrode, diameter 1 mm	[4]
Pt	Powder	[28]
Pt/C	10 wt. %, carbon supported <sup>a</sup>	[1]
Pt/C	40 wt. %, carbon supported <sup>a</sup>	[32]
Pt/C	60 wt. %, carbon supported <sup>a</sup>	[28]

<sup>a</sup> Carbon type not given.

Table 4  
AB<sub>2</sub>- and AB<sub>5</sub>-type hydrogen storage alloys as anode electrocatalysts for the DBFCs

Electrocatalyst	Alloy type	Reference
LaNi <sub>4.5</sub> Al <sub>0.5</sub>	AB <sub>5</sub>	[16]
LmNi <sub>4.78</sub> Mn <sub>0.22</sub>	AB <sub>5</sub> (Lm is La-richened mischmetal)	[17,19]
LmNi <sub>4.78</sub> Mn <sub>0.22</sub> , Si modified	AB <sub>5</sub> (Si 10 wt.%)	[17]
M <sub>m</sub> Ni <sub>3.2</sub> Al <sub>0.2</sub> Mn <sub>0.6</sub> Co <sub>1.0</sub>	AB <sub>5</sub>	[36]
M <sub>m</sub> Ni <sub>3.2</sub> Al <sub>0.2</sub> Mn <sub>0.6</sub> B <sub>0.03</sub> Co <sub>1.0</sub>	AB <sub>5</sub>	[36]
M <sub>m</sub> Ni <sub>3.55</sub> Al <sub>0.3</sub> Mn <sub>0.4</sub> Co <sub>0.75</sub>	AB <sub>5</sub> (mischmetal La–30 wt.%, Ce–50 wt.%, Nd–15 wt.%, Pr–5 wt.%)	[20,36,37]
M <sub>m</sub> Ni <sub>3.6</sub> Al <sub>0.4</sub> Mn <sub>0.3</sub> Co <sub>0.7</sub>	AB <sub>5</sub> (mischmetal La–30 wt.%, Ce–50 wt.%, Nd–15 wt.%, Pr–5 wt.%)	[38]
M <sub>m</sub> Ni <sub>4.5</sub> Al <sub>0.5</sub>	AB <sub>5</sub>	[36]
ZrCr <sub>0.8</sub> Ni <sub>1.2</sub>	AB <sub>2</sub>	[34]
Zr <sub>0.9</sub> Ti <sub>0.1</sub> Mn <sub>0.6</sub> V <sub>0.2</sub> Co <sub>0.1</sub> Ni <sub>1.1</sub>	Surface-treated Zr–Ni Laves AB <sub>2</sub>	[35]
Zr <sub>0.9</sub> Ti <sub>0.1</sub> V <sub>0.2</sub> Mn <sub>0.6</sub> Cr <sub>0.05</sub> Co <sub>0.05</sub> Ni <sub>1.2</sub>	AB <sub>2</sub>	[36]

ysis can play an important role in fuel cell devices. For the Amendola et al.'s study [21], Au particles were electrochemically deposited on carbon cloths and a low magnification SEM showed that gold particles were fairly identical, highly dispersed and uniformly distributed: particle diameter roughly about 500 nm, with agglomerates up to about 4  $\mu\text{m}$ . The colloidal metal synthesis according to the so-called Bönnerman method with the modifications introduced by Götz and Wendt [41] was the way chosen by Gyenge and workers [12–14] for their catalysts: Au, Au–Pt, Au–Pd, Pt, Pt–Ni, Pt–Ir, Os, Os–Sn, Os–Mo, Os–V. As this method was known to produce nanoparticles with sizes of 1–10 nm [41], Gyenge and co-workers [13] supposed the production of nanodiameters for their Au-based catalysts:  $\sim 6$  nm for Au–Pt and Au–Pd particles and  $\sim 10$  nm for Au particles. Feng et al.'s [22] used nanosized Au (10–20 nm by TEM) to avoid the borohydride hydrolysis. Ponce-de-León et al. [23] deposited gold on titanate nanotubes (Au/TiO<sub>2</sub>) by ion exchange adsorption and chemical reduction. By this procedure, it was produced evenly distributed spherical Au nanoparticles with a diameter of  $\sim 4$  nm (TEM image) while no large or isolated particles were observed. This nanosized Au/TiO<sub>2</sub> had promising catalytic activity: it carried twice the electrical charge compared to the commercial Au/C during the oxidation of borohydride (electrical charge per unit Au loading: 8320 and 3940 mC mg<sup>-1</sup> cm<sup>-2</sup>, respectively). The Cheng et al. [24,25] choice fell upon the impregnation method for preparing their carbon-supported Ag, Au, Ni, Pd and Pt catalysts but no precise information about the metallic particles size is given. In fact, there is no publication directly dealing with the preparation method effects on the anode performance. There is also a lack concerning the physical characterization of the catalysts. It is essential to make good these lacks because such studies might solve many issues in the electrocatalysts area. Whatever the preparation method may be, it seems to have a consensus about the need of having nanosized catalyst particles.

Kim et al. [28] investigated carbon-supported Pt and bulk Pt electrocatalysts and remarked that the performances of the 1.5 mg cm<sup>-2</sup> Pt/C and 6 mg cm<sup>-2</sup> Pt anodes were comparable. This result was a first step towards the reduction of the Pt content and the anode catalyst cost, even if a complete replacement of the noble metal will be more favourable to increase the DBFC competitiveness [29]. Franco et al. [42] proposed a first picture

of their work where a gold-plated platinum catalyst offered a better discharge curve than both platinum and gold-plated nickel (these catalysts are not reported in Tables 2 and 3 because of no clear information about their origin) and avoided the borohydride hydrolysis. The authors asserted they were working on the modification of the plating procedure to enhance the anode performance.

Suda co-workers [30] investigated the effects of the anode modification on the hydrogen evolution rate and on the cell performance. Their modification procedure was quite original for the present fuel cell since the authors prepared their anode by mixing Ni powder with carbon-supported precious metals (10 wt.% Ag, Au or Pd on Vulcan XC-72). The addition of Pd/C to Ni depressed the hydrogen evolution rate and improved the DBFC performances. The addition of Ag/C or Au/C depressed also the hydrogen evolution rate and even more effectively than that of Pd/C, but degraded the DBFC performances.

Deshmukh and Santhanam [43] were the first scientists to propose a support different from the active carbon. Their anode was constructed with platinized–functionalized multiwalled carbon nanotubes, which gave 180% higher current and about 5% more voltage output than the Au–Pt/C catalyst of Amendola et al. [21]. Unfortunately, the authors did not compare the performances of their carbon nanotube-based anodes to carbon black-based electrode they could have prepared themselves. The comparison would have been direct and consistent because the study would have been realised with the same experimental setup in identical operating conditions. More recently, Ponce-de-León et al. [23] chose the titanate nanotubes TiO<sub>2</sub> as support for a gold-based electrocatalyst. The authors adopted this material for many reasons: (i) high surface area, i.e. 250 m<sup>2</sup> g<sup>-1</sup> (Vulcan XC-72 active carbon, 240 m<sup>2</sup> g<sup>-1</sup>), (ii) good ion exchange properties, (iii) possibility of supporting up to 10 wt.% of a precious metal catalyst, providing an even distribution of the metal nanoparticles.

Another important feature of the carbon-supported electrocatalyst is the metal loading. Unfortunately, no paper deals with it and the differences in the experimental conditions make any comparison of papers quite difficult. To illustrate these words, one can regard the works of Gyenge et al. [13] and Cheng and Scott [24]. For both, the anode catalyst was Au/C and the cathode one was Pt/C. Details about the electrocatalysts and other conditions are given in Table 5. Their respective polarization data

Table 5  
Comparison tryout of two different investigations

	Gyenge and co-workers's work [13]	Cheng and Scott's work [24]
Anode Electrocatalyst	20 wt.% Au/C, 5 mg cm <sup>-2</sup>	60 wt.% Au/C, 2 mg cm <sup>-2</sup>
Cathode Electrocatalyst	20 wt.% Pt/C, 4 mg cm <sup>-2</sup>	60 wt.% Pt/C, 2 mg cm <sup>-2</sup>
Cell temperature	25 °C	25 °C
Anolyte	8 wt.% NaBH <sub>4</sub> in aqueous, 8 wt.% NaOH, 85 ml min <sup>-1</sup>	5 wt.% NaBH <sub>4</sub> in aqueous, 10 wt.% NaOH, 10 ml min <sup>-1</sup>
Oxidant	O <sub>2</sub> , 200 ml min <sup>-1</sup> , 2.7 atm	O <sub>2</sub> , 200 ml min <sup>-1</sup> , 1 atm
Open Circuit Potential	~1.1 V	~1.1 V
Current density when 0 V	50 mA cm <sup>-2</sup>	100 mA cm <sup>-2</sup>

showed that the cell voltage reached the 0 value for a current density of 50 mA cm<sup>-2</sup> [13] and 100 mA cm<sup>-2</sup> [24]. It is to note that better performances are generally expected for electrocatalysts with higher metal content: 20 wt.% [13] versus 60 wt.% [24]. It is really difficult to compare and quantitatively discuss such results.

To summary, the poor anodic efficiency of borohydride obstructs the DBFC development. The restriction of the borohydride hydrolysis is a key point in order to increase the coulombic efficiency of the cell, which can be increased by improvements of the anode material surface properties and characteristics [8]. This implies further efforts in the optimization of the catalyst preparation procedure. Gold shows promising electrocatalytic activity as anodic material if its particles are nanosized. Besides, binary alloys of noble metals involving gold provide worthwhile results. Gyenge et al. [13] showed that alloying Au, a metal that has to the maximum eight-electron oxidation of borohydride, with Pd or Pt, well-known dehydrogenation catalysts, improved the electrode kinetics of borohydride oxidation. Otherwise, Kim et al. [28] suggested that the improvement of the cell performance required modifying the anode microstructure. The catalyst support is also an area to investigate because of the great possibilities offered by the high surface area materials.

## 2.2. Anolyte

The DBFC fuel is an aqueous solution of hydroxide and borohydride because this last is stable in alkaline media. The influences of both electrolyte and fuel have been already well investigated as described by the Lakeman and co-workers' review [6]. The borohydride solution must be kept alkaline. Kim et al. [28] showed that the performance of the DBFC was improved with increasing the pH up to 14. Gardiner and Collat [44] proposed ratio between the hydroxide and borohydride concentrations superior to 4.4. Chatenet et al. [15,45] remarked that more than 100 times hydroxide compared to borohydride was necessary, because at low hydroxide concentration, e.g. BH<sub>4</sub><sup>-</sup>/OH<sup>-</sup> ratio equal to 1, the borohydride oxidation was limited and the borohydride ions were spontaneously hydrolyzed into BH<sub>3</sub>OH<sup>-</sup>. However, Cheng and Scott [24] reported that the NaOH concentration had a relatively small effect on the DBFC performance compared to the NaBH<sub>4</sub> concentration and concluded that both concentrations should be optimized. Hence, as the DBFC systems are different from one laboratory to the

other, each one requires an optimization of the liquid feed and the existing knowledge can make this easier.

Additives known for their inhibiting effect on the hydrogen evolution can be added to the fuel. This can be a solution to reduce the borohydride hydrolysis. Gyenge et al. [4,12] investigated both thiourea and tetraethylammonium hydroxide. Thiourea inhibited the borohydride hydrolysis and so the hydrogen evolution. However, the borohydride oxidation in presence of thiourea remained a four-electron process instead of the maximum eight-electron that could have been expected [4,12]. In fact, the oxidation of borohydride could not go to completion based on eight electrons exchanged due to the lack of adsorbed hydroxide on the electrode surface as required by Eq. (1). This is a half-success but a first step in the improvement of the DBFC performance. Nevertheless, one can note here that sulphur is a severe poison for the metallic catalysts and the S atom of the thiourea (H<sub>2</sub>N–CS–NH<sub>2</sub>) presents then a non-negligible risk of catalyst deactivation [46,47]. Franco et al. [42] suggested as well that additives could be added to both anolyte and catholyte in order to reduce the overpotentials associated with the borohydride oxidation and the hydrogen peroxide reduction, H<sub>2</sub>O<sub>2</sub> being for their DBFC the oxidant. Nevertheless, it will be also interesting to check if such compounds would not be at the origin of any unexpected negative effect.

## 3. Second main issue: borohydride crossover

### 3.1. Membrane electrolyte

One of the roles of the membrane electrolyte is to prevent the borohydride ions contact with the cathode where the electrocatalyst can be active towards borohydride. There are two types of membranes: the anion exchange membrane and the cation exchange membrane. For the DBFC, the anion exchange membrane ideally transports the hydroxide ions while the cation exchange membrane transports the sodium (or potassium) cations. Two reviews [6,7] provide an interesting discussion about the membranes. On the one hand, Lakeman and co-worker's review [6] especially discusses issues of both types of membrane. On the other hand, Wee's review [7] deeply discusses the cation exchange membrane.

The great majority of the fuel cells used the cation exchange membrane and more particularly the Nafion<sup>®</sup> membrane (from DuPont) [1,4,12–14,16,17,19,24,27,29,31,35–38,42,48–51]. Its selection rather than the anion exchange membrane had two

reasons: (i) the Nafion<sup>®</sup> membrane was expected to prevent the borohydride anion crossover and (ii) it showed better mechanical and chemical stabilities in strong alkaline environment.

There are actually two papers dealing with laboratory-prepared membranes. Lakeman et al. [52] tested 12 cation exchange membranes prepared by radiation grafting and two Nafion<sup>®</sup> membranes. The novel membranes showed resistance of an equal magnitude to the commercial ones. Very recently, Cheng et al. [53] reported the performances of several radiation grafted ion membranes (styrene grafted polyethylenetetrafluoroethylene, acrylic acid grafted polytetrafluoroethylene, and acrylic acid grafted low density polyethylene membranes). The first membrane showed better performances than the other membranes that included the Nafion<sup>®</sup>117 one. This better performance was attributed to the high ion exchange capacity and the high conductivity of this membrane even if it was highly permeable to borohydride (more than four times higher than that occurring with the Nafion<sup>®</sup> membrane). In fact, nowadays the investigations about the DBFCs are not really devoted to the synthesis of membranes.

For the membrane of the DBFC, the great issue is the borohydride crossover that “naturally” takes place with the anion exchange membrane and, unfortunately, that occurs with the cation exchange membrane. The membrane for the DBFC must allow an efficient OH<sup>-</sup> transport while it must simultaneously block the BH<sub>4</sub><sup>-</sup> transport. Shukla and co-workers [38] reported a DBFC system using the Nafion<sup>®</sup>961 membrane and explained their choice by the improved properties of this material, which, unlike the most commonly used Nafion<sup>®</sup>117, mitigated the crossover. One can also keep in mind the possibility to construct a DBFC operating without membrane [6]. This is the choice of Wang and Xia [20] who preferred an alkaline electrolyte, i.e. a NaBH<sub>4</sub> solution in aqueous NaOH. This “new type of DBFC”, as defined by the authors, does not need the use of expensive ion exchange membrane.

### 3.2. Cathode electrocatalyst

Interestingly, Suda and co-workers [5,8] underlined the absence of publications regarding the cathode and suggested that many non-noble metals, such as Ni and Ag, could be usable in the DBFC thanks to their excellent anti-corrosive property against the alkaline electrolyte. Nevertheless, they recently reported that the Pt cathode had better performance stability than the Ag one [51]. It is to note that the cathode generally used is the Pt/C-catalyzed electrode [29,34–36,48,49].

The main issue for the cathode catalyst is its deactivation due to the borohydride crossover through the membrane. The efforts for hindering the crossover are focused on the membrane and also on the cathode electrocatalyst.

Suda and co-workers [29] and Cheng et al. [25] investigated the effect of Pt loading in the cathode. The cell performance was not so sensitive to Pt loading, what is interesting from a cost point of view. Nevertheless, Pt is an expensive material and its complete replacement would be more favourable. Hence, the first authors [29] have tested Ag. A cell using a 1.6 mg cm<sup>-2</sup> Ag cathode achieved maximum power densities

similar to a cell constructed with the 1.0 mg cm<sup>-2</sup> Pt cathode, what suggested that Ag was an applicable cathode catalyst for the DBFC. This work does not provide any information related to the catalyst deactivation. The second authors [25] tested Ag and Ni and noticed that their performances were encouraging despite lower performances than Pt. Moreover, the Pt and Ag cathodes showed better stabilities than both Pd and Ni. At 70 °C and at 50 mA cm<sup>-2</sup>, after 50 h, the performance of the membrane–electrodes-assembly (MEA) constructed with Pt as cathode decreased from ~0.7 to ~0.65 V while the one constructed with Ag decreased from ~0.5 to ~0.4 V.

An alternative to Pt is manganese dioxide. Verma et al. [54,55] showed by cyclic voltammetry that the MnO<sub>2</sub> catalyst was electroactive for the oxygen reduction. Feng et al. [22] constructed a simple DBFC with a MnO<sub>2</sub>-catalyzed air cathode and an Au-catalyzed anode. MnO<sub>2</sub> exhibited considerable electroactivity for oxygen reduction and showed indiscernible catalytic activities for both electrooxidation and chemical hydrolysis of borohydride. This catalyst was borohydride-resistant. Thus it should be possible to construct a simple and efficient DBFC without the need of a special ion exchange membrane or a noble metal catalyst [22]. Recently, Chatenet et al. [15,56] simultaneously published two papers. The second one, called Part II, was devoted to the kinetic of oxygen reduction on five catalysts, i.e. 10 wt.% Pt/C, 10 wt.% Au/C, 10 wt.% Ag/C, 20 wt.% MnO<sub>x</sub>/C and 20 wt.% MnO<sub>x</sub>-Mg/C. The authors particularly investigated the performances of the catalysts in parallel to their resistance towards borohydride. Pt/C showed the best activity but it was not usable with traces of borohydride in solution. It was also the case for both Au/C and Ag/C. Unaffected by the presence of borohydride, the MnO<sub>x</sub>-based materials were suitable cathode electrocatalysts. This last result is in agreement with the works of Verma et al. [54,55]. With MnO<sub>2</sub>, similar results are obtained by Wang and Xia [20].

Another alternative to Pt is iron tetramethoxy phenyl porphyrin (FeTMPP) [50]. This material was compared to 60 wt.% Au/C, Ni/C and Pt/C. In borohydride-free solution, Pt was the best cathode catalyst and Pt > FeTMPP > Ag > Ni. However, in borohydride-present solution, Pt and Ag showed poor borohydride tolerance while FeTMPP could be seen as a borohydride-tolerant material: FeTMPP > Ag > Ni > Pt. Cheng and Scott [50] concluded that the use of FeTMPP or Ag would reduce the catalyst cost in the DBFC.

The oxidant is generally oxygen but hydrogen peroxide was also used [36,37,42,48]. While Franco et al. [42] and Shukla and co-workers [36,48] used, respectively, Pt and Pt/C as cathode for the reduction of H<sub>2</sub>O<sub>2</sub>, Raman and Shukla [37] studied FeTMPP and lead sulphate (Pb/SO<sub>4</sub>). These last authors asserted that their study opened new possibilities to develop cost-effective fuel cells.

The studies about the cathode electrocatalysts are at the early beginning. This component faces two issues. The one is economic since it concerns the replacement of Pt. The other is the catalyst deactivation, which is caused by the borohydride ions crossover through the membrane. The crossover will be important so as the membrane will not be highly selective and

that's why the investigations must also focus on the catalysts. Even if Pt is the most common cathode catalyst, the published results, particularly those of Chatenet et al. [56], obviously show that it has to be avoided. The alternative solution does not seem to be the Au or Ag noble metals [56]. As shown by Verma et al. [54,55] and Chatenet et al. [56], MnO<sub>2</sub> seems to be a promising material. It provides solutions, even 'partial', to two issues of the DBFC, namely the resistance of the cathode to the deactivation and a lower cost of the catalytic material. 'Partial' because the crossover remains unsolved.

### 3.3. Anolyte

Kim et al.'s [28] investigated the influence of the borohydride concentration and remarked that the high concentrations of borohydride (>0.5 M) favoured the crossover. Furthermore, Cheng and Scott [24] observed that the high concentrations promoted high degrees of crossover and hydrolysis of borohydride despite improvements of the anode reaction rate and of the cell conductivity.

Regarding the two issues of the DBFC that are the crossover and the cost, the anolyte is a key component. As underlined by many studies, optimization of the anolyte parameters is required. The hydroxide and borohydride concentrations must be optimized, what will partially hinder the crossover. In fact, the crossover of the borohydride ions can certainly be reduced by a conjunction of improvements. These ones can be the fuel optimization, the resistance of the cathode catalyst and/or the high selectivity of the membrane.

## 4. Third main issue: DBFC cost

This third main issue of the DBFC, namely the cost issue, is succinctly developed through the previous sections.

Briefly, the DBFC is an expensive fuel cell system and that is an important issue for viewing the commercialisation of the system. This high cost is inherent to (i) the anode and cathode electrocatalysts, especially when Pt is used, (ii) the sodium borohydride raw material [7] and (iii) the membrane. All of these components are in fact very expensive. Interestingly, Wee [7,11] reviews the cost issue in two different papers and concludes that the DBFC system as portable and mobile application suffers from its high cost.

A reduction of the DBFC cost can be achieved by: (i) replacing, partly or better totally, the Pt material used as catalyst at both anode and cathode; (ii) optimizing the borohydride fuel use efficiency, what supposes a lowering of both borohydride hydrolysis and borohydride crossover; (iii) reducing the sodium borohydride raw material cost, by either a new and cheaper production process or a mass production; and (iv) reducing the membrane cost, by either producing a new and cheaper membrane or a mass production.

Since Wee [7,11] widely discussed the DBFC cost issue, the present section will not be developed anymore. As a conclusion, one can resume Suda and co-workers [5] with the following sentence: the fuel contribution to cost of electricity for the DBFC is 100 times compared with hydrogen gas.

## 5. Other issues

### 5.1. Performances of the DBFCs

Lakeman and co-workers [6] devoted a large section of their review to the DBFC performances, where some typical results were reported. However, as stressed by the authors, both discussion and comparison are very difficult because of differences in operating conditions, lacks of some experimental information and non-disclosure of the timescale for the data collection. For these reasons and because Lakeman and co-workers [6] already reviewed the DBFC performances, the goal of the present section is to briefly summarize, from an experimental point of view, the tests that were performed and published.

The DBFC performances can be evaluated at different experimental conditions: catalyst nature [14,25,36], catalyst loading [28,54], borohydride concentration [24,36,49], hydroxide concentration [24,28,36,49,55], fuel pH [28], temperature [13,14,24,35–37,48], anolyte flow rate [13,24], membrane nature and thickness [29], binder content [28], anode diffusion layer features [32].

An interesting application is to separately monitor the polarizations of the anode and the cathode [36,48,49]. By this way, Shukla and co-workers [36] remarked that the cathode was responsible of the overall potential decrease and the temperature increase improved the cathode potential. The DBFC was cathode-limited. This observation is important because it throws light on a weak point of the fuel cell.

Park et al. [32] examined the effects of the anode diffusion layer features on the cell performances. They tested Toray carbon papers with different thickness (100–370 μm) and with different polytetrafluoroethylene (PTFE) content (0–30 wt.%). These two parameters were critical. The most stable and highest performance was obtained with the thinnest PTFE-free layer, which meant that thin diffusion layer with high wet-ability was desirable. The results were striking as the maximum power densities decreased from 152 to 62 mW cm<sup>-1</sup> by increasing the PTFE content from 0 to 30 wt.% (thickness of 190 μm) and the maximum power densities decreased from 144 to 55 mW cm<sup>-1</sup> while increasing the diffusion layer thickness from 100 to 375 μm (PTFE content of 20 wt.%). In order to interpret their results, the authors considered the fuel diffusion and the hydrogen evolution. They observed that the hydrogen evolution had an adverse effect on the fuel diffusion by occupying the diffusion paths. Even if the presence of PTFE in the diffusion layer was favourable for the release of hydrogen, an adequate fuel diffusion using an appropriate diffusion layer was more important for the DBFC performance than the release of hydrogen. This study is very interesting as it stresses on the importance of the materials involved in the cell construction. They can deeply influence the system performances. This is also valid by regarding the impact on the cell performances of the preparation methods. All the steps during the DBFC construction are crucial:

- (i) Catalysts preparation, e.g. nature and content of the active metal, size and dispersion of the particles, nature of the support (Sections 2.1 and 3.2).

- (ii) Electrodes preparation, e.g. procedure for the catalyst ink preparation, nature of the binder used for the catalyst ink and its content [28], temperatures (of drying, calcination and/or sintering), procedure for the formation of the catalyst layer.
- (iii) Diffusion layer, e.g. nature, thickness, PTFE content [32] (Section 5.1.).
- (iv) Membrane, e.g. nature, thickness, chemical and thermal resistance, resistance towards crossover (Section 3.1.).
- (v) Membrane pre-treatment step prior to the MEA fabrication.
- (vi) MEA pressing: procedure, pressure, temperature, and duration.
- (vii) MEA conditioning prior to the performance tests (e.g. cationic Na<sup>+</sup> form for the cation exchange membrane).
- (viii) Bipolar plates, e.g. raw materials, physical and electrical characteristics, channels.

All of these parameters (list possibly not exhaustive) must be investigated and optimized. The published papers report, in the most part, feasibility works even if few ones deal with such optimizations. For example, Kim et al. [28] studied the effects of the Nafion<sup>®</sup> binder contents; the binder was used for the anode catalyst ink preparation.

Among all the available power data, Suda and co-workers [5,8] published one of the best performances with 290 mW cm<sup>-2</sup> at 60 °C. Miley et al. [9,10] recently achieved 600 mW cm<sup>-2</sup> for a BH<sub>4</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> DBFC. This last power density is the highest ever published for the DBFC technology but is to underline the use of H<sub>2</sub>O<sub>2</sub> as oxidant instead of O<sub>2</sub>, this latter having been used by Suda and co-workers [5,8].

## 5.2. Performance stability

Suda and co-workers [35] showed that their DBFC with a surface-treated Zr–Ni Laves alloy AB<sub>2</sub> as anode (0.2 g cm<sup>-2</sup>) and Pt as cathode (2 mg cm<sup>-2</sup>) was capable of stable operation for 29 h (200 mA cm<sup>-2</sup>, 60 °C, 0.2 L min<sup>-1</sup> of 10 wt.% NaBH<sub>4</sub> in 20 wt.% NaOH, and 0.2 L min<sup>-1</sup> of humidified O<sub>2</sub> (1 atm)). The cell voltage oscillated between ~0.55 and ~0.65 V, the data being collected each hour. Cheng and Scott [24] monitored their DBFC durability over a longer period, i.e. up to 150 h (20 mA cm<sup>-2</sup>, 25 °C, 0.01 L min<sup>-1</sup> of 5 wt.% NaBH<sub>4</sub> in 10 wt.% NaOH, 0.2 L min<sup>-1</sup> of O<sub>2</sub> (1 atm)). The anode and cath-

ode catalysts are 60 wt.% Au/C (2 g cm<sup>-2</sup>) and 60 wt.% Pt/C (2 g cm<sup>-2</sup>), respectively. The DBFC showed high initial performance (~0.67 V) and, after an initial potential drop, maintained a relatively stable performance (<0.5 V) for a period up to 150 h. The authors explained the initial performance deterioration by changes in the catalyst states, in the membrane function, in the fuel supply, in the oxidant supply and in the products removal. The comparison of the operation conditions of these two studies [35,24] shows important differences, regarding the temperature, the current density, the fuel flow rate, the operation time and the electrodes (catalyst nature and loading). In fact, the conditions set by Suda and co-workers [35] were more favourable with e.g. higher temperature [24] and higher flow rate [32]. Cheng and co-workers [25] monitored the durability of their DBFCs at a higher temperature, i.e. 70 °C. This study showed that MEAs constructed with either 60 wt.% Pt/C or 60 wt.% Au/C were quite stable over 50 h while MEAs constructed with Ni, Ag or Pd (60 wt.% on C) were not.

Cheng and Scott [50] investigated the cathode stability of their DBFC constructed with FeTMPP, Ag, Ni or Pt electrocatalysts. They recorded the cell voltage for 50 h of operation. While the cell with the Ni cathode was unstable, the cells with the FeTMPP, Ag and Pt cathodes showed comparable activities and stabilities. In another study, the Pd cathode was unstable but better than the Ni cathode [25].

The stability test provides an evaluation of the whole system and further tests are required to identify more precisely the reasons of any stability lost (e.g. anode or cathode catalyst deactivation [50], membrane deterioration). For example, the following propositions may improve the stability test: (i) longer tests would be closer to the real operating conditions; and, (ii) in order to approach the real conditions of operation, a test program where variations of temperature, current density and anolyte/oxidant flow rates might be applied.

## 5.3. Oxidant

The oxidant of the DBFC is generally O<sub>2</sub>. Either pure O<sub>2</sub> or O<sub>2</sub> from air can be used, better performances being achieved with pure O<sub>2</sub> [24,50]. Generally, the main subject related to the cathode compartment is either the catalyst [5,22,29,54–56] or an alternative to O<sub>2</sub>. As Franco et al. [42], Shukla and co-workers [36] reported the performance results of an alkaline DBFC using H<sub>2</sub>O<sub>2</sub> as oxidant (Table 6) and a maximum power density of

Table 6  
Thermodynamic and energy characteristics of the DBFC using H<sub>2</sub>O<sub>2</sub> as oxidant

	(Na <sup>+</sup> )BH <sub>4</sub> <sup>-</sup> /O <sub>2</sub>	(Na <sup>+</sup> )BH <sub>4</sub> <sup>-</sup> /H <sub>2</sub> O <sub>2</sub>	(Na <sup>+</sup> )BH <sub>4</sub> <sup>-</sup> /H <sub>2</sub> O <sub>2</sub> (H <sup>+</sup> ) <sup>a</sup>
Fuel molecular weight (g mol <sup>-1</sup> )	37.832	37.832	37.832
Oxidant molecular weight (g mol <sup>-1</sup> )	31.999	34.015	34.015
Electrons number <sup>b</sup>	8	8	8
Electromotive force (V)	1.64	2.11	3.01
Theoretical specific energy (Wh kg <sup>-1</sup> )	9295	11959	17060
Pure compound capacity (Ah kg <sup>-1</sup> )	5668	5668	5668
Conversion efficiency (%)	0.91	0.97	0.97

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> in acidic medium.

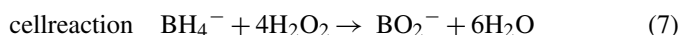
<sup>b</sup> Number of electrons involved during the direct oxidation.



150 mW cm<sup>-2</sup> at a cell voltage of 540 mV while operating at 70 °C. The direct reduction of H<sub>2</sub>O<sub>2</sub> has a standard potential of 0.87 V versus SHE:

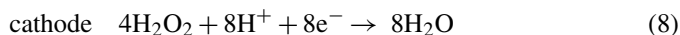


Consequently, the theoretical cell potential with H<sub>2</sub>O<sub>2</sub> is 2.11 V (1.64 V with O<sub>2</sub>):

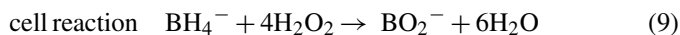


The use of H<sub>2</sub>O<sub>2</sub> provides a 30% higher theoretical specific energy for the corresponding fuel cell than the O<sub>2</sub>-based DBFC (11,959 and 9295 Wh kg<sup>-1</sup>, respectively). This is a first advantage. The use of such oxidant extends the operation of the DBFC to locations with limited air convection (e.g. underwater applications). This is a second advantage. These works are very promising and further studies are required to optimize this technology, what will also enable to check eventual issues due to H<sub>2</sub>O<sub>2</sub>.

The same group of authors [48] investigated the H<sub>2</sub>O<sub>2</sub> reduction in acidic medium (pH of 0, 0.5 and 1), where H<sub>2</sub>O<sub>2</sub> was reduced into water (standard potential of 1.77 V versus SHE) (Table 6):



The theoretical potential of the overall reaction is increased with a value of 3.01 V, what implies a higher theoretical energy density (17,060 Wh kg<sup>-1</sup>):



The authors reported a maximum power density of about 350 mW cm<sup>-2</sup> at a cell voltage of ~1 V while operating at 70 °C and concluded about the high potential of this DBFC that could reach voltages near 3 V. In a very recent paper, these authors [38] reported a power density of 28 W for a six-cell direct borohydride-H<sub>2</sub>O<sub>2</sub> fuel cell stack operating at 25 °C.

The best performance ever reached was reported by Miley et al. [9,10]. Their borohydride-H<sub>2</sub>O<sub>2</sub> fuel cell showed a maximum power density of more than 600 mW cm<sup>-2</sup>. Furthermore, the authors showed the feasibility of a 14-cell stack producing a power of 500 W.

Wee [7] and Lakeman and co-workers [6], in their respective review, did not view the oxidant among the remaining challenges of the DBFC systems. On the one hand, Wee [7] did not regard any aspect of the cathode components as being liable to obstruct the DBFC development. On the other hand, Lakeman and co-workers [6] only stressed on the improvements that are required for the oxygen cathode.

#### 5.4. Temperature effect

Cheng and Scott [24] reported that the DBFC could work in a broad range of temperatures and even at ambient temperature it was capable to deliver high-energy capacities. The authors concluded that that satisfied the necessary conditions for the use as portable power sources. Suda [8] agreed and added that the

electrochemical reaction proceeded under low temperature conditions reaching the ambient temperature. From thermodynamic data, it is to note that the electromotive force does not markedly vary with the temperature variation in the 25–85 °C range [57].

Like for other low-temperature fuel cells, the temperature increase has positive effects on cell performances [13,35,36], e.g. 20 and 63 mW cm<sup>-2</sup> at ambient and 70 °C, respectively [21]. Cheng and Scott [24,50] worked on the influence of the operating conditions and evaluated the performance of their DBFC at 25, 50, 70 and 85 °C. According to their discussion [24], the improvement of the performances with the temperature increase was due to better mass transport and improved kinetics of borohydride oxidation. Besides, the temperature increase had positive effects on the conductivity of the borohydride-hydroxide solution, as stressed by Shukla and co-workers [36] as well. Nevertheless, it had also negative effects, i.e. increase of crossover and borohydride hydrolysis, deterioration of the cathode performance, decrease of the fuel efficiency, decrease of the membrane performance due to partial drying out and poor rehydration. The increase in the hydrolysis reaction with the temperature was firstly reported by Suda and co-workers [35] who observed that, at a current of 1 A, the hydrogen evolution rate was multiplied by a factor 5 when the temperature increases from 25 to 60 °C. Furthermore, Suda and co-workers [5] showed that the fuel utilization decreased from 62% to 51% with a temperature increase of 10 °C due to both borohydride hydrolysis and crossover. Further, they [30] added that low operation temperature was good for reducing the hydrogen evolution, even with some penalty for the cell performances. A significant rate of borohydride hydrolysis at temperatures above 70 °C was previously reported by Okinaka [26]. Above all, the beneficial effects outmatched the negative ones [58].

Lastly, Cheng and Scott [50] have more especially studied the temperature effect (25–85 °C) on the cathode activity. The temperature increase had a positive effect on the cell performance thanks to several factors: combined effect of reducing the electrode potentials, increase in the electrode reaction rates, decrease of the cell resistance and decrease in the cathode channel blocks by the increased water evaporation.

The DBFC is a technology mainly devoted to mobile and portable applications and the reported performance data seem to show that the necessary conditions for its commercial use are reached [24]. The DBFC must operate in a broad range of temperature, what depends on the electronic device, the outside temperature and the country of utilization. The great majority of the papers report experimental studies performed from room temperature, except one at temperatures from 5 °C [27]. This last work showed that, despite similar open circuit voltages, the potential -0.7 V was reached at 50, 200 and 600 mA cm<sup>-2</sup> at 5, 20 and 40 °C, respectively. Hence, a question is asked: what could be the overall performance of the DBFC at temperatures much lower than 25 °C? A fuel cell as a power generation device for portable application should efficiently operate at winter temperatures without the need of a secondary power generator. It would be interesting to know the cell performances and also the catalysts, the fuel and the membrane behaviours at such low tem-

Table 7

The remaining challenges and the three main issues (borohydride hydrolysis, borohydride crossover and cost) of the DBFC

Remaining challenges	Reference	Issue <sup>a</sup>
Development of anode electrocatalysts to generate eight electrons utilized per borohydride and to inhibit the H <sub>2</sub> evolution	[5–7]	Hydrolysis
Optimization of the NaBH <sub>4</sub> aqueous solution to reduce the H <sub>2</sub> evolution	[7]	Hydrolysis
Development of electrocatalysts tolerant to deactivation	[6,7]	Crossover
Reduction of the NaBH <sub>4</sub> aqueous solution volume	[7]	Cost
Development of MEAs tolerant to crossover	[7]	Crossover
Up to 500 mW cm <sup>-2</sup> of operation power density is needed	[7]	
Treatment of the NaOH accumulation at the cathode and the NaBO <sub>2</sub> accumulation at the anode	[6–8]	
Design of cell for simple fuel maintenance	[7]	
Adjustments in electrode and cell structures to inhibit the H <sub>2</sub> evolution	[7]	Hydrolysis
Fuel cost	[5,7]	Cost

<sup>a</sup> The remaining challenges are classified according to the three main issues but they can also be seen as other issues.

Table 8

Potential solutions to the three main issues of the DBFC

Issue	Solutions for the			
	Anode catalyst	Cathode catalyst	Fuel/anolyte	Membrane
Borohydride hydrolysis	Au-based		Optimization H <sub>2</sub> generation inhibitor additive <sup>a</sup>	
Borohydride crossover		MnO <sub>2</sub>	Optimization	More selective <sup>b</sup> No membrane
DBFC cost	No Pt Au-based Hydrogen storage alloys	No Pt MnO <sub>2</sub>	Optimization NaBH <sub>4</sub> mass production Inhibition of borohydride hydrolysis and crossover	More selective <sup>b</sup> Cheaper No membrane

<sup>a</sup> The addition of such additive implies an increase of the fuel cost but this could be recouped if the fuel was more efficiently used.

<sup>b</sup> A more selective membrane will be certainly more expensive than the current ones but the cost could be recouped if the fuel was more efficiently used and the membrane was mass-produced.

peratures. Even if the temperature does not seem to be an issue, some dark points should be highlighted, i.e. cell behaviour at low temperatures and efficiency when starting at low temperatures.

## 6. Potential solutions to the main issues and conclusions

The DBFC development is obstructed by mainly three issues. Wee [7] reviewed the remaining challenges. Table 7 groups them but also those quoted by Suda and co-workers [5] and Lakeman and co-workers [6]. Among the 10 challenges that are suggested, seven are relative to the three main issues (i.e. borohydride hydrolysis, crossover and DBFC cost). There are real opportunities for improvements [6]. The previous sections give an insight of the potential solutions. It is possible to summary them (Table 8).

The borohydride hydrolysis issue is the most studied. The solution may be a combination of improvements related to the anode catalyst and the fuel (Table 8). The Au-based catalysts catalyze the borohydride oxidation by involving seven–eight electrons (Table 9). The optimization of the fuel features may contribute to the reduction of the hydrolysis. These possibilities may reduce drastically the hydrolysis and enable the direct eight-electron oxidation.

The inhibition of the borohydride crossover is considered as the key issue by Wee [7]. The best solution is a highly selective membrane; however, it occurs with both types of ion exchange membrane. In fact, a combination of improvements (membrane,

Table 9

Number of electrons transferred during the borohydride direct oxidation for the anode catalysts tested through the literature

Electrons number <i>n</i> range	Catalysts	Electrons number <sup>a</sup>	Reference
7 ≤ <i>n</i> ≤ 8	Au/C	8	[15,45]
	Pt–Au/C	8	[14]
	Pt/C	8	[1]
	Ag	7.6	[15,45]
	Au	7.6	[58]
	AB <sub>5</sub> <sup>b</sup>	7.5	[20]
	Au	7.4	[15,45]
6 ≤ <i>n</i> < 7	Au	7	[4]
	Au	6.9	[21]
	Pd/C	6	[1]
	Pt/C	6	[1]
4 ≤ <i>n</i> < 6	Ag	6	[31]
	Au	4.5	[1]
	Pt–Ni	4.5	[4]
	Cu	4	[1]
	Ni	4	[1,27]
	Raney Ni	4	[1]
	Pd/C	4	[1]
< 4	Pt	4	[4]
	AB <sub>2</sub> <sup>c</sup>	4	[51]
	AB <sub>5</sub> <sup>b</sup>	4	[6,19,51]
	Pt	2–4	[6,28]

<sup>a</sup> Experimentally determined.

<sup>b</sup> AB<sub>5</sub>-type hydrogen storage alloy.

<sup>c</sup> AB<sub>2</sub>-type hydrogen storage alloy.

fuel and cathode catalyst) is certainly the best way to efficiently hinder the crossover (Table 8). It seems difficult even impossible to completely avoid it with the current membranes. The combination of a more resistant cathode catalyst (e.g. MnO<sub>2</sub>) with a more resistant membrane [38] may be a solution. Otherwise, one can keep in mind to construct a membrane-free fuel cell [6,20].

The DBFC is expensive. It would be competitive if the crossover and the borohydride hydrolysis were to be overcome [7]. A decrease of the catalysts cost may be achieved. The sodium borohydride will be cheaper if its mass production increases. In the same time, its production cost must be drastically reduced [7]. The solutions proposed to overcome the previous two issues consider the cost issue, i.e. cheaper catalysts, fuel optimization, utilization of additives, more resistant membrane and more efficient use of the fuel.

The DBFC technology interests more and more but it is still in the development phase and there are several problems to solve. As underlined by Lakeman and co-workers [6], there is relatively small number of years of R&D invested in DBFCs and there are real improvement opportunities. The published works mainly deal with the three issues that are the borohydride hydrolysis (occurring instead of its direct oxidation), the borohydride crossover and the DBFC cost. Other issues must be also overcome, such as e.g. catalysts ageing or metabolite removing (Table 8). Regarding this last problem, Suda [Suda-2006] particularly stressed on the need of removing the accumulated NaBO<sub>2</sub>, which, because of its low solubility, can precipitate and lead to a fatal decrease of the electric capacity. Besides, Suda [8] regarded the volume occupied by the fuel tanks, cartridges or canisters as a serious problem and concluded that the DBFC was not suitable as alternative power sources for the secondary batteries such as the Ni–MH and Li-ion batteries because of their overall volume-based energy density.

Above all, facing issues during the research and the development of a new and innovative technology is ‘normal’. As no one has doubts about overcoming these issues, there is a consensus about the promising future of the DBFC as a commercial portable power generator system.

## References

- [1] B.H. Liu, Z.P. Li, S. Suda, *Electrochim. Acta* 49 (2004) 3097.
- [2] M.E. Indig, R.N. Snyder, *J. Electrochem. Soc.* 109 (1962) 1104.
- [3] R. Jasinski, *Electrochem. Technol.* 3 (1965) 40.
- [4] E. Gyenge, *Electrochim. Acta* 49 (2004) 965;  
E. Gyenge, *Electrochim. Acta* 49 (2004) 1875.
- [5] Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Alloys Compd.* 404–406 (2005) 648.
- [6] C. Ponce-de-León, F.C. Walsh, D. Pletcher, D.J. Browning, J.B. Lakeman, *J. Power Sources* 155 (2006) 172.
- [7] J.H. Wee, *J. Power Sources* 155 (2006) 329;  
J.H. Wee, *J. Power Sources* 160 (2006) 514.
- [8] S. Suda, *Encyclopaedia of Materials: Science and Technology*, Elsevier Ltd., 2006, pp. 1–4.
- [9] G.H. Miley, *Proceedings of the 8th Annual Small Fuel Cells—Small Fuel Cells for Portable Applications*, Washington, DC, United States of America, 2006.
- [10] G.H. Miley, N. Luo, J. Mather, R. Burton, G. Hawkins, L. Gu, E. Byrd, R. Gimlin, P.J. Shrestha, G. Benavides, J. Laystrom, D. Carroll, *J. Power Sources* 165 (2007) 509.
- [11] J.H. Wee, *J. Power Sources* 161 (2006) 1.
- [12] M.H. Atwan, D.O. Northwood, E.L. Gyenge, *Int. J. Hydrogen Energy* 30 (2005) 1323.
- [13] M.H. Atwan, C.L.B. Macdonald, D.O. Northwood, E.L. Gyenge, *J. Power Sources* 158 (2006) 36.
- [14] E. Gyenge, M.H. Atwan, D.O. Northwood, *J. Electrochem. Soc.* 153 (2006) A150.
- [15] M. Chatenet, F. Micoud, I. Roche, E. Chainet, *Electrochim. Acta* 51 (2006) 5459.
- [16] L. Wang, C. Ma, X. Mao, J. Sheng, F. Bai, F. Tang, *Electrochem. Commun.* 7 (2005) 1477.
- [17] L. Wang, C. Ma, X. Mao, *J. Alloys Compd.* 397 (2005) 313.
- [18] B.H. Liu, S. Suda, *J. Alloys Compd.*, 2007, doi:10.1016/j.jallcom.2006.12.034.
- [19] L. Wang, C. Ma, Y. Sun, S. Suda, *J. Alloys Compd.* 391 (2005) 318.
- [20] Y.G. Wang, Y.Y. Xia, *Electrochem. Commun.* 8 (2006) 1775.
- [21] S.C. Amendola, P. Onnerud, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman, M. Binder, *J. Power Sources* 84 (1999) 130.
- [22] R.X. Feng, H. Dong, Y.D. Wang, X.P. Ai, Y.L. Cao, H.X. Yang, *Electrochem. Commun.* 7 (2005) 449.
- [23] C. Ponce-de-León, D.V. Bavykin, F.C. Walsh, *Electrochem. Commun.* 8 (2006) 1665, and references therein.
- [24] H. Cheng, K. Scott, *J. Power Sources* 160 (2006) 407.
- [25] H. Cheng, K. Scott, K.V. Lovell, *Fuel Cells* 6 (2006) 367.
- [26] Y. Okinaka, *J. Electrochem. Soc.* 120 (1973) 739.
- [27] B.H. Liu, Z.P. Li, S. Suda, *J. Electrochem. Soc.* 150 (2003) A398.
- [28] J.H. Kim, H.S. Kim, Y.M. Kang, M.S. Song, S. Rajendran, S.C. Han, D.H. Jung, J.Y. Lee, *J. Electrochem. Soc.* 151 (2004) A1039.
- [29] B.H. Liu, Z.P. Li, K. Arai, S. Suda, *Electrochim. Acta* 50 (2005) 3719.
- [30] Z.P. Li, B.H. Liu, J.K. Zhu, S. Suda, *J. Power Sources* 163 (2006) 555.
- [31] E. Sanlı, H. Çelikkan, B.Z. Uysal, M.L. Aksu, *Int. J. Hydrogen Energy* 31 (2006) 1920.
- [32] K.T. Park, U.H. Jung, S.U. Jeong, S.H. Kim, *J. Power Sources* 162 (2006) 192.
- [33] C. Ponce-de-León, F.C. Walsh, A. Rose, J.B. Lakeman, D.J. Browning, R.W. Reeve, *J. Power Sources* 164 (2007) 441.
- [34] S.M. Lee, J.H. Kim, H.H. Lee, P.S. Lee, J.Y. Lee, *J. Electrochem. Soc.* 149 (2002) A603.
- [35] Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Electrochem. Soc.* 150 (2003) A868.
- [36] N.A. Choudhury, R.K. Raman, S. Sampath, A.K. Shukla, *J. Power Sources* 143 (2005) 1.
- [37] R.K. Raman, A.K. Shukla, *J. Appl. Electrochem.* 35 (2005) 1157.
- [38] R.K. Raman, S.K. Prashant, A.K. Shukla, *J. Power Sources* 162 (2006) 1073.
- [39] J. Wang, B.E. Koel, *J. Phys. Chem. A* 102 (1998) 8573.
- [40] M. Haruta, *Chem. Rec.* 3 (2003) 75.
- [41] M. Götz, H. Wendt, *Electrochem. Acta* 43 (1998) 3637.
- [42] M.W. Franco, J.A.D. Condeço, C.A.C. Sequeira, *Proceedings of the 209th ECS Meeting, 2006*, [www.electrochem.org/meetings/biannual/209/209.htm](http://www.electrochem.org/meetings/biannual/209/209.htm).
- [43] K. Deshmukh, V.K.S. Santhanam, *J. Power Sources* 159 (2006) 1084.
- [44] J.A. Gardiner, J.W. Collat, *J. Am. Chem. Soc.* 87 (1965) 1692.
- [45] M. Chatenet, F. Micoud, E. Chainet, *Proceedings of the 209th ECS Meeting, 2006*, [www.electrochem.org/meetings/biannual/209/209.htm](http://www.electrochem.org/meetings/biannual/209/209.htm).
- [46] U.B. Demirci, *Electrochim. Acta* 52 (2007) 5119.
- [47] E. Gyenge, *Electrochim. Acta* 52 (2007) 5122.
- [48] R.K. Raman, N.A. Choudhury, A.K. Shukla, *Electrochem. Solid State Lett.* 7 (2004) A488.
- [49] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, *J. Power Sources* 126 (2005) 28.
- [50] H. Cheng, K. Scott, *J. Electroanal. Chem.* 596 (2006) 117.
- [51] B.H. Liu, S. Suda, *J. Power Sources* 164 (2007) 100.
- [52] J.B. Lakeman, A. Rose, K.D. Pointon, D.J. Browning, K.V. Lovell, S.C. Waring, J.A. Horsfall, *J. Power Sources* 162 (2006) 765.

- [53] H. Cheng, K. Scott, K.V. Lovell, J.A. Horsfall, S.C. Waring, *J. Membr. Sci.* 288 (2007) 168.
- [54] A. Verma, A.K. Jha, S. Basu, *J. Power Sources* 141 (2005) 30.
- [55] A. Verma, S. Basu, *J. Power Sources* 145 (2005) 282.
- [56] M. Chatenet, F. Micoud, I. Roche, E. Chainet, *Electrochim. Acta* 51 (2006) 5452.
- [57] <http://www.grc.nasa.gov/WWW/CEAWEWeb>.
- [58] H. Cheng, K. Scott, *Electrochim. Acta* 51 (2006) 3429.