



Review

Which type of fuel cell is more competitive for portable application: Direct methanol fuel cells or direct borohydride fuel cells?

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Abstract

The promise of fuel cell systems using liquid fuels, such as the direct methanol fuel cell (DMFC) and direct borohydride fuel cell (DBFC), to complement or substitute for existing batteries is becoming recognized, along with their potential as a future technology for mobile and portable power supplies. The key issue is which type of fuel cell is more competitive for such power supplies: DMFC or DBFC? To answer this question, the present study analyzes and discusses the relative competitiveness of these two systems given the current status of the technologies and assuming some generally accepted conditions. The findings confirm that the DBFC system is superior to the DMFC system in terms of cell size and fuel (or fuel solution) consumption. Thus, the DBFC system is better suited to applications that require small operational space. On the other hand, the total operating costs of DBFC systems are higher than those of DMFC systems. According to the total cost formulae derived in the analysis, the DBFC system becomes relatively uneconomic at higher power outputs and longer operation times, but may be more favourable in specific portable applications such as miniaturized or micro power systems with short operational time spans.

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Keywords: Direct methanol; Fuel cell; Sodium borohydride; Portable power supply; Methanol; Hydrogen**Contents**

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1. Introduction

With the rapid development of mobile communications and mobile Internet technology, the market for portable electronic devices is certain to experience continued growth. At present, the power supplies used for portable appliances are mostly rechargeable Li- or Ni-based battery systems. Given the rapid development of Li-based battery technology over the past decade, this system has succeeded in dominating supply applications in markets such as laptop computers, mobile phones, and personal digital assistants.

In the current portable appliance market, there is growing pressure on battery manufacturers to increase specific energy for the next generation of portable electronic equipment. For example, here is a growing technological requirement for high bandwidth applications that demand much more power. The situation is becoming critical as mobile phones and laptop computers merge to provide users with broadband wireless and multifunctional, portable computing capability. With these developments, Li-based or other rechargeable battery systems are not suitable for high power and long lifespan portable devices due to their limited specific energy and operational time [1–4]. Therefore, a fuel cell system using a liquid fuel has become recognized as having the potential to complement or substitute batteries and promises to develop into a future technology for mobile and portable power supplies [4–11].

While there are several types of fuel cell using liquid fuel, a direct methanol fuel cell system (DMFC) with methanol (MeOH) as the fuel is considered to be the most promising candidate for portable and mobile applications and has consequently attracted world-wide research due to the ready availability of MeOH as a fuel [12–19]. Despite the many advantages of the DMFC systems for practical use, several drawbacks need to be overcome such as low efficiency, low power density, MeOH crossover (or permeation), and CO₂ generation [12,13]. These hurdles will incur some delay before the successful and economical commercialization of DMFC systems.

In addition to the DMFC systems, the direct borohydride fuel cell (DBFC) system, with NaBH₄ solution as the fuel has attracted attention since the late 1990s for application in portable power supplies due to its higher specific energy and more compact structure than the DMFC system. Despite obstacles such as the high price of NaBH₄, hydrogen generation and the treatment of by-products generated during operation [11,20,21], many researchers have advocated the suitability of the DBFC as an alternative system for portable applications [11,22–29]. Although many studies have examined DMFC and DBFC [10,24,27,30,31], it appears that a comparison of their relative merits has not been reported. Thus, such an evaluation is the central focus of the present paper.

The analysis is carried out by comparing important parameters such as fuel and fuel solution consumption in terms of mass and volume, water and gases generated, fuel cartridge volume, and fuel chamber volume. Finally, the total cost of each system, i.e., cell manufacturing and fuel consumption costs, is calculated to determine the more favourable technology.

2. Direct methanol fuel cell

2.1. Research history

The DMFC system was first recognized in 1922 by the German researcher Müller, who studied the electro-oxidation of MeOH. By 1951, Kordesch and Marko had begun construction of a DMFC based on Müller's early concept. Interest in DMFCs was further aroused about a decade later, with a new focus on military applications. Alkaline electrolytes were tested by researchers at Allis-Chalmers in 1963. A DMFC based on an aqueous acid electrolyte, which does not react with CO₂ produced at the anode, was developed by researchers at Esso and Shell in 1965. Esso constructed a 100-W DMFC system for powering communication equipment. Shell found Pt–Ru to be most effective as an anode electrocatalyst, and produced a 300-W prototype system in 1968. There was little further progress until 1992, when DuPont's Nafion proton-exchange membrane (PEM) was found to be far superior to the old sulfuric acid medium. In 1994, the Jet Propulsion Laboratory in California demonstrated a Nafion-based DMFC, and in the following dozen years there was a new developmental wave of DMFC systems based on the PEM electrolyte [13,32].

In 1996, Ren et al. [33] constructed and tested several DMFC systems that had a liquid feed and were operated under different conditions with varieties of Nafion [33]. The best performances were obtained at a high temperature of 130 °C, but this is too high for portable power sources [13,32].

Following an extensive research effort world-wide, the DMFC has recently passed the demonstration phase to enter partially the commercialization stage. Many companies working in the fields of fuel cell technology (Antig, Neah Power Systems, DMFC Corp., DTI energy, INI Power, MTI MicroFuel Cells, Energy Visions Inc., Plug power, Smart Fuel Cell), communications and electricity (NTT, Toshiba, Motorola, Fujitsu, Sanyo, Samsung, IBM) have developed DMFCs for various portable applications, as well as prototypes systems that use on-board DMFCs [4,34–36].

2.2. Technology status

In a DMFC, as shown in Fig. 1, the liquid MeOH fuel is oxidized in the presence of water at the Pt–Ru anode elec-

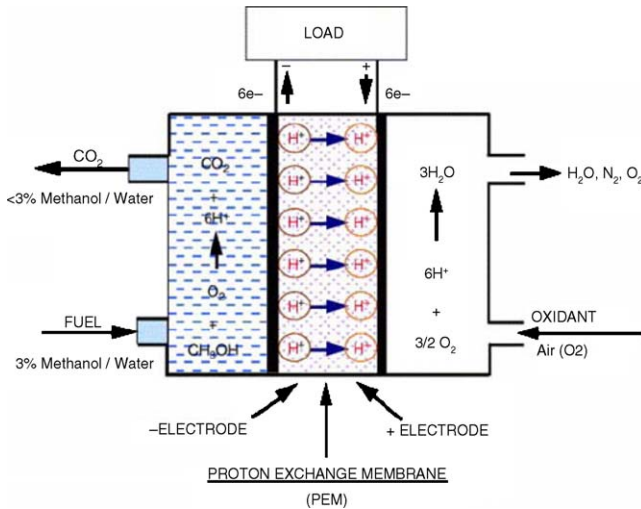
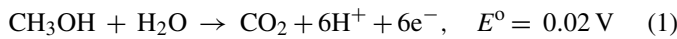


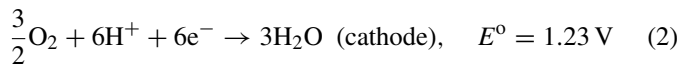
Fig. 1. Schematic diagram of DMFC system (a top view) [60].

trrocatalyst. This results in the generation of CO₂, hydrogen ions and electrons that travel through the external circuit as the electric output of the fuel cell. The hydrogen ions are conducted through the electrolyte (e.g., Nafion), and react with oxygen from the air at the Pt cathode electrocatalyst, and the electrons from the external circuit form water at the cathode to complete the circuit. Thus, the DMFC reactions are as follows:

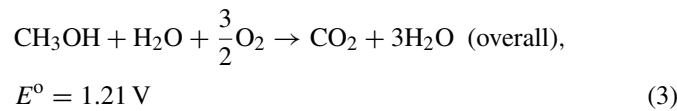
At anode (negative electrode):



At cathode (positive electrode):



Overall:



Note all potentials in this paper are reported with respect to the standard hydrogen electrode (SHE). The typical operational voltage of a single DMFC cell ranges from 0.4 to 0.6 V. In portable devices, the maximum power density generally delivered is restricted within the range of 20 to 50 mW cm⁻² at an operational voltage of 0.5 V [12,37]. This performance is the generally accepted value when operating the DMFC with 1–2 M MeOH as the fuel at a temperature of 60 °C and at atmospheric pressure. Recently, however, DMFC power densities of 100–200 mW cm⁻² have been reported [4,12,38–40]. The performances were measured, however, at operating conditions that are considered to be relatively unsuitable for portable applications, namely at high levels of temperature, MeOH concentration and pressure.

3. Direct borohydride fuel cell

3.1. Research history

The DBFC system was first proposed in the early 1960s [41,42]. Indig and Snyder [41] reported a practical demonstration of direct electricity generation from borohydride ions. Research on DBFC technology then stagnated until the late 1990s. In 1999, Amendola et al. [22] reported the performance of a DBFC system that used an Au–Pt alloy electroplated on carbon cloth as the anode, while the cathode was a commercial gas-diffusion electrode and was separated from the anode by an anode electrolyte membrane.

Following further impressive research efforts over the next 5 years [11,22–27], the first demonstration of a DBFC system for laptop computers was presented in 2005 by the Materials and Energy Research Institute (MERIT) [43]. MERIT succeeded in increasing the DBFC system output from 10 to 400 W. Recent vigorous research on DBFCs has greatly raised the expectation for the realization of the various benefits promised by this fuel cell system for portable applications.

3.2. Technology status

There are three types of DBFC as determined by the choice of electrolyte [11]. When potassium hydroxide solution or an anion-exchange membrane (AEM) is employed as the electrolyte, the cathode-to-anode transfer of OH⁻ ions functions as both the charge carrier and the ion migration. On the other hand, in DBFC systems with a cation-exchange membrane (CEM) electrolyte such as Nafion, Na⁺ migrates from the anode to the cathode to carry the charges. While each system has its own advantages and disadvantages, the CEM electrolyte supports the most efficient DBFC system in terms of the NaBH₄ crossover [11,23] and is therefore adopted in the DBFC system investigated in this review.

The CEM–DBFC system directly uses the NaBH₄ solution, with the chamber fuel either being pre-filled into, or continuously supplied to, the chamber at each anode compartment, as shown in Fig. 2.

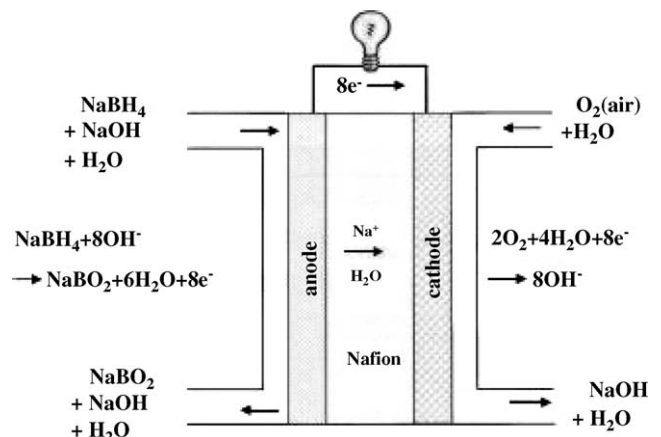


Fig. 2. Schematic diagram of DBFC system (a top view) [26].

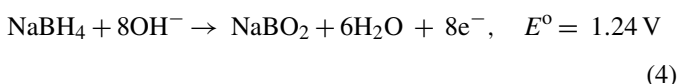
Table 1
Performance and properties of DMFC and DBFC systems used to evaluate their competitiveness

Performance and properties	DMFC	DBFC [11]
Power density (mW cm^{-2})	80 [48]	290 [11]
Operational voltage (V)	0.5	1.0
Operating temperature ($^{\circ}\text{C}$)	~ 60	~ 60
Fuel solution	1 and 2 M MeOH	10% NaBH_4 –20% NaOH aqueous solution
Oxidant	O_2 (air)	O_2 (air) and water
Electrolyte	Nafion	Nafion
Anode electrocatalyst	Pt-based Ru	$\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1}$
Cathode electrocatalyst	Pt	Pd
Amount of fuel crossover ($\times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$)	4.00	4.01 [27]

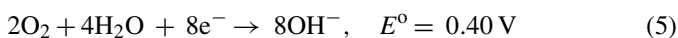
Taken from state-of-the-art systems and traditionally accepted values.

Electricity is produced via the following anode and cathode reactions Eqs. (4) and (5), to give the overall reaction Eq. (6):

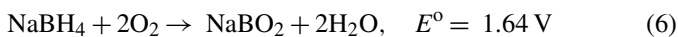
Anode (negative electrode):



Cathode (positive electrode):



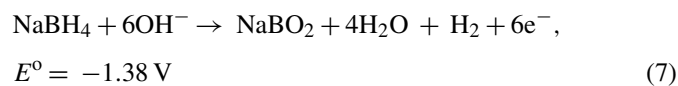
Overall:



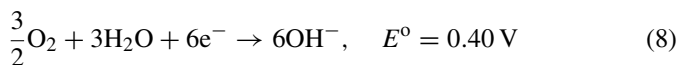
Although one BH_4^- ion can generate eight electrons in the theoretically complete DBFC system, as shown in Eq. (4), the number of electrons is inevitably less in real systems. The most influential factor is the anode electrocatalyst system. The reported number of electrons generated per BH_4^- ion is 6.9 with an Au catalyst [22], 6 with a Pd catalyst [44], and 4 with a Ni catalyst [45].

In the DBFC system generating six electrons, the following undesirable reactions, including H_2 generation, proceed:

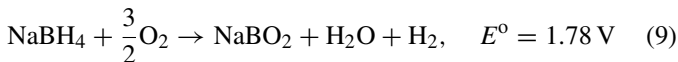
Anode (negative electrode):



Cathode (positive electrode):



Overall:



Therefore, the issues of how to obtain a complete, eight-electron reaction and how to restrain H_2 evolution are currently two of the key problems to solve in achieving practical application of DBFCs.

Many studies have reported [11,22–27,46] that DBFC power density ranges from 20 to 290 mW cm^{-2} at operational voltages of 1 to 1.5 V and at a temperature below 85 $^{\circ}\text{C}$. Interestingly, Miley [47] has recently achieved a power density of 600 mW cm^{-2} for a DBFC system that uses H_2O_2 [47].

4. Comparative analysis of the performance and properties of DMFC and DBFC systems

The performance and the other properties of DMFC and DBFC systems are listed in Table 1 and include values from both state-of-the-art systems and traditionally accepted data.

4.1. Power density

The power density values for each fuel cell are based on state-of-the-art values. When functioning as the power supply for portable devices, the DMFC system should be operated below 60 $^{\circ}\text{C}$ and at atmospheric pressure. Under these conditions, the state-of-the-art DMFC delivers 80 mW cm^{-2} [48]. One study [48] on technology from Neah power systems has demonstrated power density levels exceeding 80 mW cm^{-2} at room temperature. Therefore, 80 mW cm^{-2} is assigned as the DMFC power density in the present analysis and therefore a calculated DMFC area of 250 cm^2 is required to produce 20 W. Although this assumed power density might be considered to be optimistically high compared with the traditionally accepted maximum power density of 50 mW cm^{-2} under the same conditions, it might be a reasonable value to evaluate the DMFC system for future applications given the rapid development of current DMFC technology. Except for the amount of MeOH crossover, traditionally accepted values are assumed for the other conditions in DMFC systems, such as the fuel solution concentration, cathode gas, electrolyte, anode electrocatalyst, and cathode electrocatalyst [12].

In the case of DBFC systems, for which there are relatively few published studies [11,22–27], research into the state-of-the-art technology has been conducted by Li et al. [11]. The authors have reported a maximum power density of 290 mW cm^{-2} at an operating voltage of 1 V with single and stacked DBFC systems, as listed in Table 1. Thus, it was claimed that a single cell area of 68 cm^2 was needed to generate 20 W of power.

4.2. Fuel crossover

It is known that liquid fuel crossover in each type of fuel cell is influenced by operating parameters such as liquid fuel concentration, cell pressure, temperature, membrane thickness, and catalyst morphology. Therefore, it is not easy to determine

the exact amount of fuel crossover in each fuel cell system under the conditions listed in Table 1.

Many investigations have dealt with the transport phenomena and MeOH crossover within DMFCs [49–57]. Reported rates of MeOH crossover have included $1.4 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ using pure Nafion membranes [49], $1.12 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ with Nafion 117 [50], $4.00 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ with composite membrane [51], and $1.32 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ with advanced membrane [52]. Recently, Silva et al. [53] predicted a value of $2.95 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ by modelling based on DMFC performance for a wide range of proton conductivities and the permeability of MeOH towards PEM. Based on all these findings, a reasonably acceptable level of MeOH crossover is in the order of $10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ and agrees well with the value of $4.00 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ listed in Table 1.

While crossover is also known to be a major issue with DBFCs, it is somewhat different from that in DMFCs. This problem cannot be solved for the AEM-DBFC system because NaBH_4 as an anion can easily permeate through an AEM. By contrast, fuel crossover is less serious in the CEM-DBFC system because the BH_4^- ion cannot permeate through a CEM due to the latter's negative charge. Furthermore, our experimental results confirm that crossover in the CEM-DBFC system is less than that in the DMFC system. Nevertheless, the NaBH_4 solution permeates from anode to cathode due to diffusion and the osmotic drag of the fuel solution. According to one investigation [27], the loss of NaBH_4 due to crossover was calculated to be $4.01 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$, even when using Nafion 117 as the CEM electrolyte. Therefore, this value is assigned (Table 1) as the amount of NaBH_4 crossover in the DBFC system chosen here for comparative evaluation with a DMFC system.

5. Comparative analysis of DMFC and DBFC systems

5.1. Theoretical and operational energy

The theoretical and operational energy of each fuel cell are listed in Table 2. For a DMFC, the theoretical specific energy is calculated to be 6.08 Wh g^{-1} of pure MeOH. This is 65% of the 9.30 Wh g^{-1} value obtained with pure NaBH_4 in the 8e-DBFC system and 20% less than that of the 6e-DBFC system [11]. The theoretical feeding rates of fuel that are required to gener-

ate 1 W are calculated to be 2.74 mg min^{-1} of pure MeOH in DMFC, 1.79 mg min^{-1} of pure NaBH_4 in the 8e-DBFC system, and 2.20 mg min^{-1} of pure NaBH_4 in the 6e-DBFC system.

In practice, the differences in specific energy and fuel consumption between the two systems become even larger due to the much lower performance of the DMFC system. Assuming that the maximum power densities can be delivered at an operational voltage of 0.5 V in the DMFC, its practical specific energy is found to be 2.51 Wh g^{-1} , which is only 44% of the 5.67 Wh g^{-1} value obtained from a 8e-DBFC system operated at 1 V, and 40% less than that of a 6e-DBFC system. These values correspond to feed rates of 6.63 mg min^{-1} of pure MeOH, and of 2.94 and 3.92 mg min^{-1} of pure NaBH_4 for the 8e- and 6e-DBFC systems, respectively, to generate 1 W without considering fuel crossover.

5.2. Comparison of fuel cell size for 20-W portable device

5.2.1. Amounts of pure fuel and fuel solution without considering crossover (theoretical values)

Based on the values listed in Table 2, the comparative amounts of pure fuels (MeOH and NaBH_4) consumed and fuel solutions required to generate a power output of 20 W are listed in Table 3. These data have been calculated without considering any fuel loss due to crossover.

For a DMFC system using 1 M MeOH solution (1 M-DMFC) as a fuel solution, 8.0 g of pure MeOH and 238.4 g of water are simultaneously needed to generate 20 W. This amount of MeOH fuel corresponds to a volume of 248.9 cm^3 . When the MeOH concentration was increased to 2 M (2 M-DMFC), the volume of fuel solution decreases to 124.4 cm^3 . The volume of fuel solution in the DBFC system is even less than that in the DMFC system. In the 8e-DBFC system, for example, only 29.6 cm^3 (or 35.3 g) of 10% NaBH_4 –20% NaOH aqueous solution, including 3.5 g of NaBH_4 , 7.1 g of NaOH and 24.7 g of water, is required to generate the same power output.

The volume of fuel solution in each fuel cell system equals the volume of the fuel solution chamber that is in direct contact with the anode electrocatalysts within the cell and this is the key factor to consider in the design of the fuel cell. Therefore, the fuel chamber in the anode compartment of the 8e-DBFC system is only 12% of that in the 1 M-DMFC and 24% of that in the 2 M-DMFC.

Table 2

Theoretical and operational energy values of each fuel cell system (without considering fuel crossover)

Theoretical and operational values	DMFC	8e-DBFC ^a	6e-DBFC ^b
Theoretical values			
Reversible voltage (V)	1.21	1.64	1.78
Specific energy (Wh g^{-1} of pure MeOH or NaBH_4)	6.08	9.30	7.57
Feeding rate of fuel to generate 1 W (mg min^{-1} of pure MeOH or NaBH_4)	2.74	1.79	2.20
Operational values			
Operational voltage (V)	0.50	1.00	1.00
Specific energy (Wh g^{-1} of pure MeOH or NaBH_4)	2.51	5.67	4.25
Feeding rate of fuel to generate 1 W (mg min^{-1} of pure MeOH or NaBH_4)	6.63	2.94	3.92

^a 8e-DBFC = 8-electron system.

^b 6e-DBFC = 6-electron system.

Table 3
Comparative amounts of pure fuel and fuel solution consumed to generate 20 W in each fuel cell system without considering fuel crossover, together with amounts of by-products

Fuels and by-products	1 M-DMFC	2 M-DMFC	8e-DBFC	6e-DBFC
Fuel and fuel solution				
Pure fuel (g or ml of pure MeOH or NaBH ₄)	8.0 (10.1) ^a	8.0 (10.1) ^a	3.5	4.7
Water for fuel solution (g)	238.4	115.2	24.7	32.9
NaOH for fuel solution (g)	0	0	7.1	9.4
Total amounts of fuel solution (g or ml)	246.4 (248.9) ^b	123.2 (124.4) ^b	35.3 (29.6) ^c	47.0 (39.5) ^c
Fuel cartridge volume ^d (ml of pure MeOH or 10% NaBH ₄ –20% NaOH)	10.1	10.1	29.6	39.5
By-products				
Water generated (g)	13.4	13.4	3.4	2.2
NaBO ₂ generated (g)	0	0	6.2	8.2
Gas generated (g or ml)	10.9 (5570) of CO ₂	10.9 (5570) of CO ₂	0	0.2 (2786) of H ₂

^a Relative density of pure MeOH = 0.79 [58].

^b Relative density of 1 and 2 M MeOH solution = 0.99 [59].

^c Relative density of 10% NaBH₄–20% NaOH solution = 1.19 [24].

^d Cartridge volume of each fuel cell system calculated when cartridge-filled pure MeOH and cartridge-filled 10% NaBH₄–20% NaOH solution are injected into DMFC and DBFC systems, respectively.

The size of the DMFC fuel cartridge can be reduced to be even smaller than that of the DBFC because the liquid fuel is pure MeOH. In other words, 10.1 ml of pure MeOH filled in a cartridge that is external to the cell body can be injected into the chamber in the form of droplets. In the case of the DBFC system using a fuel cartridge, because of the solid NaBH₄, the fuel has to be supplied to the user in solution form. Therefore, the required volume of the DBFC cartridge is the same as that of the fuel solution chamber, i.e., 29.6 ml.

5.2.2. Water and gas generation

While some of the water generated in each fuel cell system during operation can be recycled as fuel solution, most must be drained out. The amount and handling of this drainage is a very important factor, when using the fuel cells in portable devices. Based on Eqs. (3), (6) and (9), the amount of water generated at a power output of 20 W are listed in Table 3. The water generated in the DMFC system is calculated to be 13.4 g, i.e., four-fold greater than the 3.4 g in the 8e-DBFC system. The amount of water generated using these two systems to generate 20 W for 10 h is shown in Fig. 3. The DBFC system is more favourable than the DMFC system in terms of less water generated.

Despite the lower water generation in the DBFC system, 0.31 g Wh⁻¹ of NaBO₂ is produced in the anode compartment in the 8e-DBFC system. Whereas most of the NaBO₂ is soluble in water and can be eliminated with the drained water, some is also slightly precipitated on the anode electrocatalyst and thereby acts as a poison. In addition, aqueous NaOH is formed in the cathode compartment and the solution therefore needs to be recovered for the fuel feeding solution.

The DMFC system also generates CO₂ during operation and this necessitates ventilation when the DMFC system is operated in a closed space. The theoretical amount of CO₂ generated in the anode compartment at a power output of 20 W is 10.9 g or 5.57 l (at standard state). In the 6e-DBFC system, 2.79 l of H₂ is generated. If, however, the 8e-DBFC system were operated as close to theoretical conditions as possible, none of these gases would be generated. As shown in Fig. 4, 55.7 l of CO₂ in the

DMFC system is produced at a power output of 20 W during 10 h.

The characteristics and quantities of the by-products can be the most important factors in assessing the competitiveness of the two fuel cell systems for portable applications. Naturally, the generation of small amounts is better. Given that greater generation of water and CO₂, DMFC systems are further inferior to the 8e-DBFC system in terms by-product generation during cell operation.

5.2.3. Fuel and fuel solution considering crossover

Considering the assumed amount of fuel crossover in each fuel cell system, as listed in Table 1, the fuel loss in the DBFC system is lower than that in the DMFC at the same power output of 20 W, presumably due to the higher potential power density

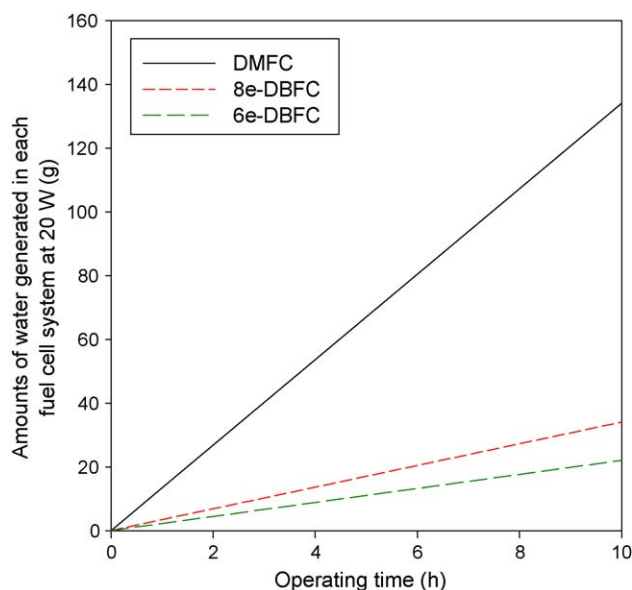


Fig. 3. Amount of water generated in each fuel cell system operated at power output of 20 W during 10 h.

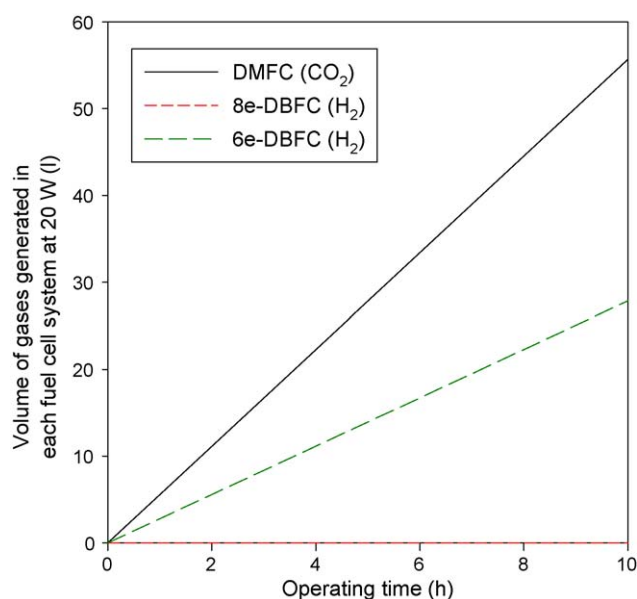


Fig. 4. Amount (volume at standard states) of gases generated in each fuel cell system operated at power output of 20 W during 10 h; CO_2 in DMFC and H_2 in DBFC.

of the DBFC. The loss of pure fuel due to crossover is 11.5 mg of MeOH in the DMFC and 3.8 mg of NaBH_4 in the DBFC at a power output of 20 W.

Therefore, when the above losses are added to the fuel consumed solely in producing power, as listed in Table 3, the actual amounts needed for operation at 20 W are 19.5 mg of pure MeOH (or 24.6 cm^3) in the DMFC and 7.3 mg of pure solid- NaBH_4 in the 8e-DBFC system (see Table 4). These results mean that the pure fuel should be fed with an excess of 145% of MeOH in the DMFC and 106% of solid- NaBH_4 in the 8e-DBFC to generate the required power output.

Next, the additional amount of water required for adjusting the fuel concentration of solution according to the fuel lost from crossover should be considered. In the DMFC system, because the pure, cartridge-filled MeOH can be used solely to make up the loss of fuel due to crossover, no additional water is needed. In the DBFC, however, because the fuel solution has to be supplied as 10% NaBH_4 –20% NaOH aqueous solution, the volume or amount is proportional to the amount of fuel crossover. There-

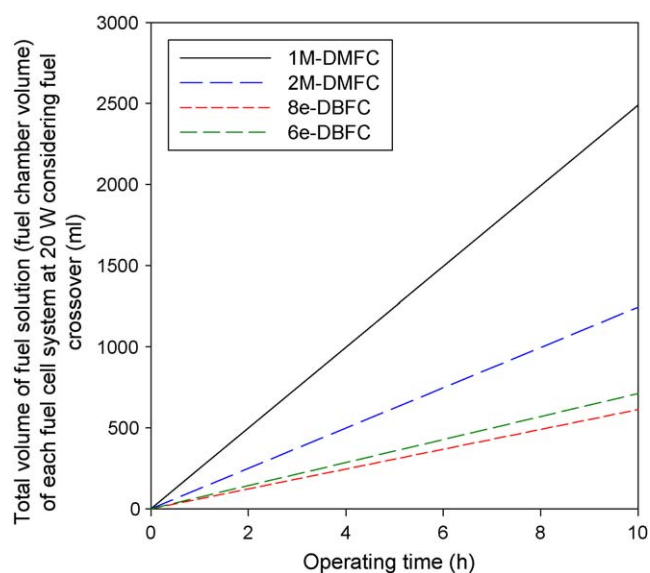


Fig. 5. Fuel solution volume (or fuel chamber volume) of each fuel cell system needed to generate power output of 20 W during 10 h considering fuel crossover; 1 or 2 M MeOH aqueous solution in DMFC and 10% NaBH_4 –20% NaOH aqueous solution in DBFC.

fore, the difference in the fuel solution volume between the two systems is reduced after taking crossover into account compared with the case without consideration of crossover.

Based on the results listed in Table 4, the volume of fuel solution in each system required to generate a power output of 20 W during 10 h is shown in Fig. 5. As mentioned above, this volume can also be regarded as the fuel chamber volume in the anode compartment when using a cartridge fuelling system. As shown in Fig. 5, the chamber volume of the 8e-DBFC is 25% of that of the 1 M-DMFC and 50% of that of the 2 M-DMFC. Naturally, the difference in fuel solution volume between the DMFC and DBFC systems increases with respect to operation time and power output.

The fuel cartridge volume of the DMFC system is smaller than that of the DBFC system (see Fig. 6). A 246-ml cartridge filled with pure MeOH is needed for 10 h operation at a 20 W power output, compared with a 612-ml cartridge filled with 10% NaBH_4 –20% NaOH aqueous solution in the 8e-DBFC system.

Table 4

Comparative amounts of pure fuel and fuel solution consumed to generate 20 W in each fuel cell system considering fuel crossover

Fuel and fuel solution	1 M-DMFC	2 M-DMFC	8e-DBFC	6e-DBFC
Pure fuel (g or ml of pure MeOH or NaBH_4)	19.5 (24.6) ^a	19.5 (24.6) ^a	7.3	8.5
Water for fuel solution (g)	238.4	115.2	58.3	67.7
NaOH for fuel solution (g)	0	0	14.6	16.9
Total amounts of fuel solution (g or ml)	246.4 (248.9) ^b	123.2 (124.4) ^b	72.9 (61.2) ^c	84.6 (71.1) ^c
Fuel cartridge volume ^d (ml of pure MeOH or 10% NaBH_4 –20% NaOH)	24.6	24.6	61.2	71.1

^a Relative density of pure MeOH = 0.79 [58].

^b Relative density of 1 and 2 M MeOH solution = 0.99 [59].

^c Relative density of 10% NaBH_4 –20% NaOH solution = 1.19 [24].

^d Cartridge volume of each fuel cell system was calculated when cartridge-filled pure MeOH and cartridge-filled 10% NaBH_4 –20% NaOH solution injected into the DMFC and DBFC systems, respectively.

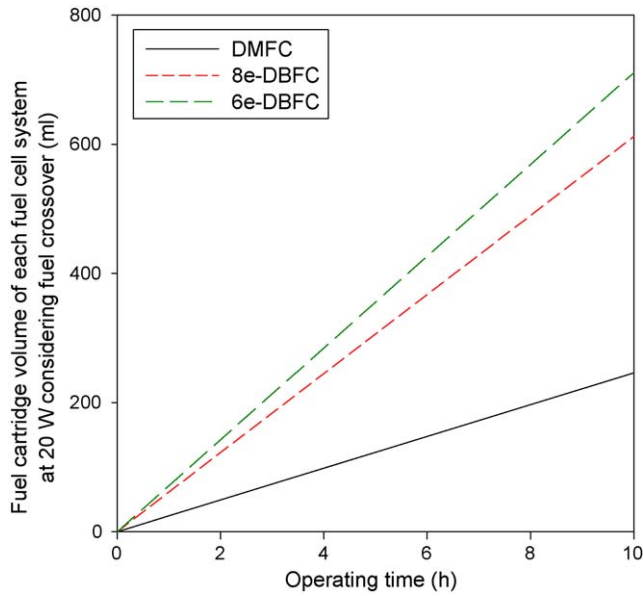


Fig. 6. Fuel cartridge volume of each fuel cell system needed to generate power output of 20 W during 10 h considering fuel crossover; cartridge-filled pure MeOH in DMFC and cartridge-filled 10% NaBH₄–20% NaOH aqueous solution in DBFC.

5.3. Total costs of DMFC and DBFC systems

5.3.1. Production costs

The production costs of typical DMFC and DBFC systems comprise those of the membranes, electrodes, bipolar plates, peripherals and assembly process. In addition, the costs of ‘non-active’ items necessary to supply, remove and treat fluids (pumps, fans, valves, humidity regulators, etc.) need to be included. It is known that the DMFC is more expensive than the DBFC, mainly due to the high costs of materials used in fabrication (especially, the platinum electrocatalysts). Furthermore, the complex cell structure required for the elimination of CO₂ generated within the cell and the fuel solution concentration sensor add to the costs. Dyer [7] reported a production cost for a DMFC system as high as \$5 per Watt (note, all costs in this study are given in US\$).

On the other hand, MERIT researchers [43] announced in 2005 that they planned to sell a 20-W DBFC system for laptop computer use at a price of \$90 in 2006. Considering that the standard formula to evaluate the manufacturing cost is one-third of the selling cost, this implies a fixed DBFC cost of \$1.5 per Watt or \$30 for a power output of 20 W. The lower production cost of DBFC might be due to its several advantages such as the use of non-Pt-based electrocatalysts and a more compact cell structure.

5.3.2. Fuel costs

The current price of MeOH fuel for DMFCs is \$10.4 per kg [35] and of NaBH₄ for DBFCs is \$55 per kg. Therefore, considering the amount of the fuel consumed to generate power output, as listed in Table 3, the cost of MeOH is \$0.0041 per W, while that of NaBH₄ is US \$0.0097 per W the 8e-DBFC system and \$0.0129 per W for the 6e-DBFC system.

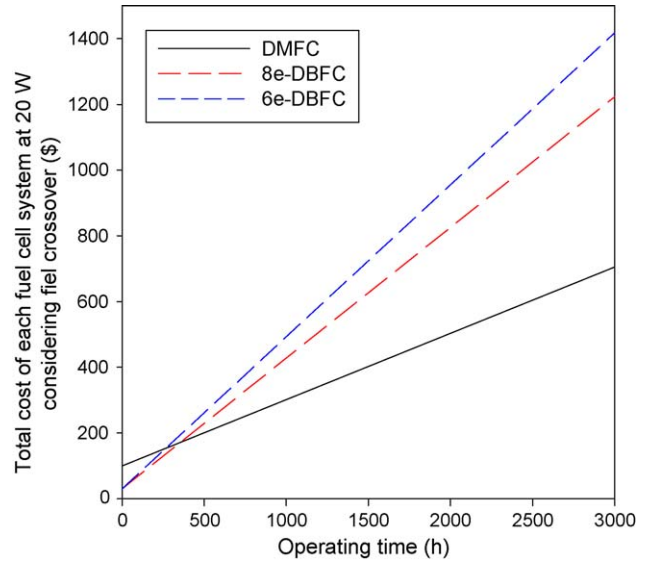


Fig. 7. Total cost of each cell system operated at power output of 20 W during 3000 h considering crossover; prices of fuels assumed to be \$10.4 kg⁻¹ (MeOH) and \$55 kg⁻¹ (NaBH₄).

Furthermore, given the amount of fuel crossover and the power density in each fuel cell system (Table 1), the additional cost of the fuel loss is calculated to be \$0.006 per W for the DMFC and \$0.0102 per W for the DBFC.

5.3.3. Total costs

Considering the production and fuel costs in each fuel cell system, the total cost of each system can be calculated using the following equations for DMFC, 8e-DBFC and 6e-DBFC systems, respectively:

$$\$_{\text{total,DMFC}} = \$5.0(W_{\text{fixed}}) + \$0.0041(W)(h) + 0.0060(W)(h) \quad (10)$$

$$\$_{\text{total,8e-DBFC}} = \$1.5(W_{\text{fixed}}) + \$0.0097(W)(h) + 0.0102(W)(h) \quad (11)$$

$$\$_{\text{total,6e-DBFC}} = \$1.5(W_{\text{fixed}}) + \$0.0129(W)(h) + 0.0102(W)(h) \quad (12)$$

In each equation, the first term is the production cost of the fuel cell system, the second is the cost of the fuel consumed for solely generating the power, and third is the cost of fuel due to crossover. In addition, W_{fixed} is the fixed power capacity of the fuel cell, W the power output in watts, and h is the operation time in h.

The total costs of each fuel cell system operated with a power output of 20 W for up to 3000 h are shown in Fig. 7. When using a portable device with a power output of 20 W continuously, the 8e-DBFC system is more competitive than the DMFC system only for operation times under 280 h. Nevertheless, the competitiveness of the 8e-DBFC system within this short operational timeframe has no practical potential for commercial operation due to a desired durability or lifespan of more 5000 h. Therefore,

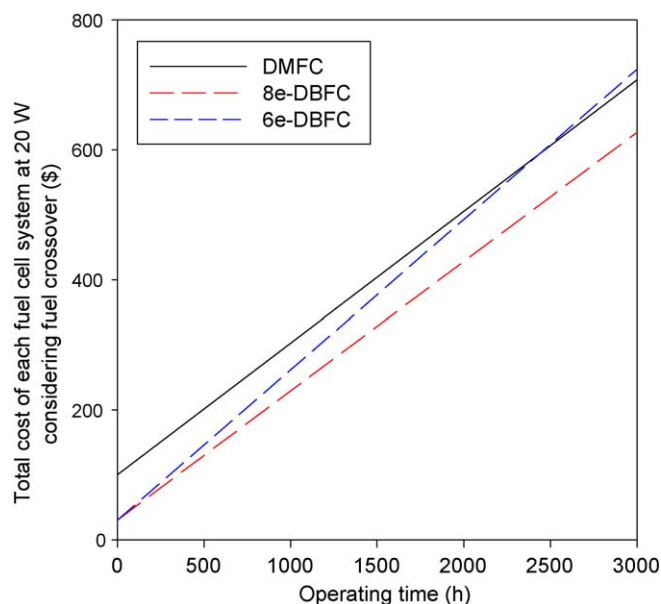


Fig. 8. Comparative total cost of each cell system operated at power output of 20 W during 3000 h considering crossover; prices of fuels assumed to be $\$10.4 \text{ kg}^{-1}$ (MeOH) and $\$27.5 \text{ kg}^{-1}$ (NaBH_4).

at the level of current technology, it is very clear that at higher power outputs and longer operation times, the DMFC system is more competitive than the DBFC system in terms of total costs. Nevertheless, the DBFC system could be more favourable in specific application fields such as for smaller or micro power systems for which short operation times are acceptable. In addition, such miniaturized application fields also require a significant reduction in cell size, for which the DBFC remains more competitive than the DMFC.

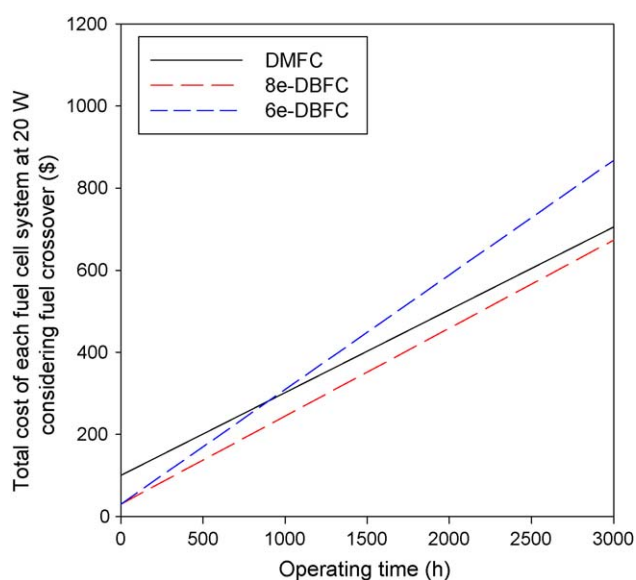


Fig. 9. Comparative total cost of each cell system operated at power output of 20 W during 3000 h considering fuel crossover in DBFC to be 4.01×10^{-8} (mol of $\text{NaBH}_4 \text{ cm}^{-2} \text{ s}^{-1}$); prices of fuels assumed to be $\$10.4 \text{ kg}^{-1}$ (MeOH) and $\$55 \text{ kg}^{-1}$ (NaBH_4).

The lower competitiveness of the DBFC system in terms of total costs is primarily ascribed to the high price of NaBH_4 . Therefore, any reduction in the price or consumed amount of NaBH_4 would make the DBFC system more competitive than the DMFC system in all portable applications. For example, at half the current price, i.e., $\$27.5 \text{ kg}^{-1}$ (NaBH_4), with all other conditions held constant, the comparative total cost of the systems can be calculated as presented in Fig. 8.

In addition, if the NaBH_4 loss due to crossover could be reduced more than that of DMFC by one order of magnitude, i.e., to 4.01×10^{-8} (mol of $\text{NaBH}_4 \text{ cm}^{-2} \text{ s}^{-1}$), the 8e-DBFC system would become the most competitive of the three fuel cell systems, as shown in Fig. 9. It should be possible to decrease substantially the NaBH_4 crossover by increasing the power density and by developing a CEM electrolyte that is more resistant to crossover.

6. Conclusions

Many factors must be considered to ascertain whether a DMFC or a DBFC is the more competitive for portable power supply systems. The present paper, first addresses some of the relative factors such as the amount or volume of consumed fuel and fuel solution, water and gases generated, and the fuel cartridge volume of each fuel cell system. The total cost of each system is then evaluated to determine the relative favourability of each fuel cell type. This analysis is based entirely on the current technologies with some generally accepted conditions being assumed.

After considering fuel crossover, the calculated amount of fuel solution (or fuel chamber volume in the anode compartment) of each fuel cell necessary to generate a power output of 20 W is 248.9 l in the 1 M-DMFC system and 61.2 l of 10% NaBH_4 –20% NaOH aqueous solution in the 8e-DBFC system. In addition, the DMFC system is relatively less competitive than the 8e-DBFC system in terms of the amount of by-products generated during the cell operation such as water and gas. This result indicates that the DBFC system could be more favourable in applications that require operation in smaller spaces. Nevertheless, the volume of the DMFC fuel cartridge can be reduced to 40% less than that for the 8e-DBFC system.

While the DBFC system could be more competitive than the DMFC system in terms of cell size and volume, its total cost for generation in real operation, considering fuel crossover, is higher than that of the DMFC. According to the equations derived in the present study to calculate their total cost, although the DBFC system is uncompetitive at higher power outputs and longer operation times, it may gain favour in specific applications such as smaller or micro power systems operated over short operation times.

The lower competitiveness of the DBFC system is primarily ascribed to the high price of NaBH_4 . If, however, this price can be reduced to half of the current amount or if the NaBH_4 loss due to crossover can be reduced more than that of DMFC by one order of magnitude, with all other conditions held constant, the 8e-DBFC system may become more competitive in terms of total cost in all portable applications.

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