

# Development of the direct borohydride fuel cell

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## Abstract

Borohydrides are a group of compounds with high hydrogen contents. For example, NaBH<sub>4</sub> contains 10.6 wt% hydrogen. The direct anodic oxidation of borohydride provides more negative potentials than that of hydrogen. One ion of BH<sub>4</sub><sup>-</sup> generates eight electrons. The theoretical energy density can reach as high as 9.3 Wh/g of NaBH<sub>4</sub> if using sodium borohydride as the fuel. The theoretical energy conversion efficiency of the DBFC (0.91) is larger than that of the PEMFC (0.83). Recently, the cell power density 290 mW/cm<sup>2</sup> has been achieved. A five-cell stack with an effective area of 67 cm<sup>2</sup> demonstrated that the power reached to 110 W when the operation temperature reached 60 °C, even if the stack operation started at room temperature without humidification.

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**Keywords:** Borohydride; Fuel cell; Anode; Cathode; Membrane

## 1. Introduction

Hydrogen is a clean energy resource. It generates energy by chemical oxidation (combustion) or electrochemical oxidation (fuel cell). Fuel cells directly convert chemical energy into electricity with high efficiency as compared with hydrogen combustion engine. They are being developed to be used in vehicles, portable and mobile devices. The polymer electrolyte membrane fuel cell (PEMFC), the alkaline fuel cell (AFC) and the phosphoric acid fuel cell (PAFC) require gaseous hydrogen as the fuel. However, hydrogen storage technologies are still on the way to match practical needs. Compressed hydrogen is considered as a feasible solution to vehicle applications but is not suitable for portable devices due to its lower volumetric energy density. Using liquid fuel is considered to be the solution to improve the volumetric energy density, but liquid fuels usually need fuel modification process that makes the fuel supply complicated. The direct methanol fuel cell (DMFC) using methanol as the fuel, is considered as a promising candidate for portable

and mobile applications but its low performance is a high hurdle to practical uses. Besides carbon hydrogen fuels, boron hydrogen compounds (borohydrides) are considered to be potential fuels for fuel cells [1–7].

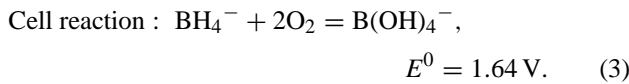
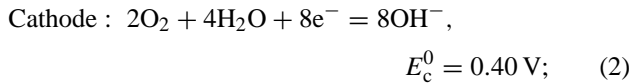
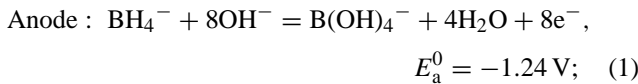
Borohydrides are a group of compounds with high hydrogen contents. For example, NaBH<sub>4</sub> contains 10.6 wt% hydrogen. It is much more than most hydrogen storage alloys have. The direct electricity generation from borohydride ion has been proved to be practical [3,4,8–11], though these mechanisms were somewhat different because different electrode materials were used. The theoretical energy density can reach up to 9.3 Wh/g of NaBH<sub>4</sub> if using sodium borohydride as the fuel, which is higher than that of methanol (6.1 Wh/g of MeOH). From engineering consideration, borohydride solution can be used as a heat exchange medium to cool fuel cell so that cooling plates are not needed in fuel cell stack. Furthermore, the electro-osmotic drag of water can be used as the cathode reactant so that the humidifier for hydrogen gas (PEMFC) or air (AFC) can be eliminated. These features are benefit to the fuel cell system design. Nowadays, the direct borohydride fuel cell (DBFC) is considered as a potential candidate for portable and mobile applications.

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## 2. Fundamental aspects of the DBFC

### 2.1. Electrochemistry of the DBFC

In principle, the electrochemical reactions of the DBFC take place under an alkaline medium because borohydride ions are not chemically stable in acidic media. The electrode reactions and cell reaction can be described as following:



$E_a^0$  stands for standard anode potential,  $E_c^0$  stands for standard cathode potential and  $E^0$  is the electromotive force (e.m.f) of the DBFC. It is very impressive that one ion of  $\text{BH}_4^-$  generates eight electrons and the e.m.f can reach to 1.64 V that is 1.33 times compared with the PEMFC and 1.35 times compared with the DMFC.

### 2.2. Thermodynamics and electrode kinetics of the DBFC

Like other fuel cells, the DBFC is an electrochemical system in which the chemical energy of the borohydride is converted directly into electrical energy with the aid of oxygen or air. The energy conversion efficiency ( $\eta$ ) can exceed the Carnot restriction but cannot reach to 100%. Fig. 1 shows the thermodynamic comparison of the DBFC with the PEMFC. It is noted that the theoretical energy conversion efficiency of the DBFC (0.91) is larger than that of the PEMFC (0.83).

It is known that the cell reaction of the fuel cell is irreversible. This irreversibility is mainly caused by four major losses (activation loss relating to electrode catalysts, fuel crossover and internal current, ohmic loss and concentration loss). It is impossible to obtain the reversible cell voltage ( $E^0 = \Delta G^0/nF$ ) due to these losses during operation. Fig. 2 shows the schematic performance curves of the PEMFC and the DBFC.  $E_M$  refers to the maximum cell voltage that is

calculated from the standard enthalpy change ( $\Delta H^0$ ) of the cell reaction ( $E_M = \Delta H^0/nF$ ).

If activation losses of the electrodes, ohmic losses and concentration losses of the DBFC were on the same level as the PEMFC with an operation voltage of 0.75 V, the DBFC would obtain 1 V of operation voltage under the similar operation conditions as shown in Fig. 2. This high operation voltage will benefit the stack and the system design for fuel cell users because the cell number can be reduced 25% compared with the PEMFC stacks.

### 2.3. Catalysts for the DBFC

The noble metals are the only selection for the electrode catalyst in the PEMFC, the PAFC and the DMFC because only noble metals can resist the corrosion from the acidic electrolyte. Unlike these fuel cells working under an acidic electrolyte, the DBFC operates under an alkaline electrolyte so that in addition to the noble metal catalysts, the catalysts used in the AFC and Ni–MH battery are also suitable for the DBFC. Lee et al. [12] has reported using a  $\text{ZrCr}_{0.8}\text{Ni}_{1.2}$  alloy (Laves phase alloy  $\text{AB}_2$ ) as the anode catalyst. They supposed a stepwise electricity generation mechanism which  $\text{ZrCr}_{0.8}\text{Ni}_{1.2}$  uptakes hydrogen from borohydride solution and then the hydrogen is electrochemically oxidized to generate electricity. Li et al. [13,14] reported a surface treated Zr–Ni Laves phase alloy  $\text{AB}_2$  ( $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Mn}_{0.6}\text{V}_{0.2}\text{Co}_{0.1}\text{Ni}_{1.1}$ ) as the anode catalyst in the DBFC. Liu et al. [15] reported a high power density has been achieved by using Ni powder (Inco type 210) as the anode material through electrochemical oxidation of borohydride.

Until now, there are no publications related to the cathode catalyst in the DBFC. However, in the alkaline electrolyte, many non-noble metals such as Ni and Ag show excellent anti-corrosive property against the electrolyte. The Siemens AFC using Raney Ag for the cathode has been successfully used in submarines in the early 1990s [16]. It is believed that Raney Ag is also usable in the DBFC.

### 2.4. Cell constitution of the DBFC

According to the electrolyte applied in the DBFC, there are three models as shown in Table 1. Models 1 and 2 are very similar because the charge carrier and ion migration

PEMFC	DBFC
<ul style="list-style-type: none"> <li>Cell reaction <math>\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})</math></li> <li><math>\Delta H^0 = -285.83 \text{ kJ/mol}</math> <math>\Delta G^0 = -237.13 \text{ kJ/mol}</math></li> <li>Electromotive force <math>E^0 = -\Delta G^0/nF = 1.23 \text{ V}</math></li> <li>Theoretical energy conversion efficiency <math>\eta = \Delta G^0 / \Delta H^0 = 0.83</math></li> </ul>	<ul style="list-style-type: none"> <li>Cell reaction <math>\text{BH}_4^-(\text{l}) + 2\text{O}_2(\text{g}) = \text{B(OH)}_4^-(\text{l})</math></li> <li><math>\Delta H^0 = -1392.26 \text{ kJ/mol}</math> <math>\Delta G^0 = -1267.56 \text{ kJ/mol}</math></li> <li>Electromotive force <math>E^0 = -\Delta G^0/nF = 1.64 \text{ V}</math></li> <li>Theoretical energy conversion efficiency <math>\eta = \Delta G^0 / \Delta H^0 = 0.91</math></li> </ul>

Fig. 1. Thermodynamic comparison of the PEMFC with the DBFC.

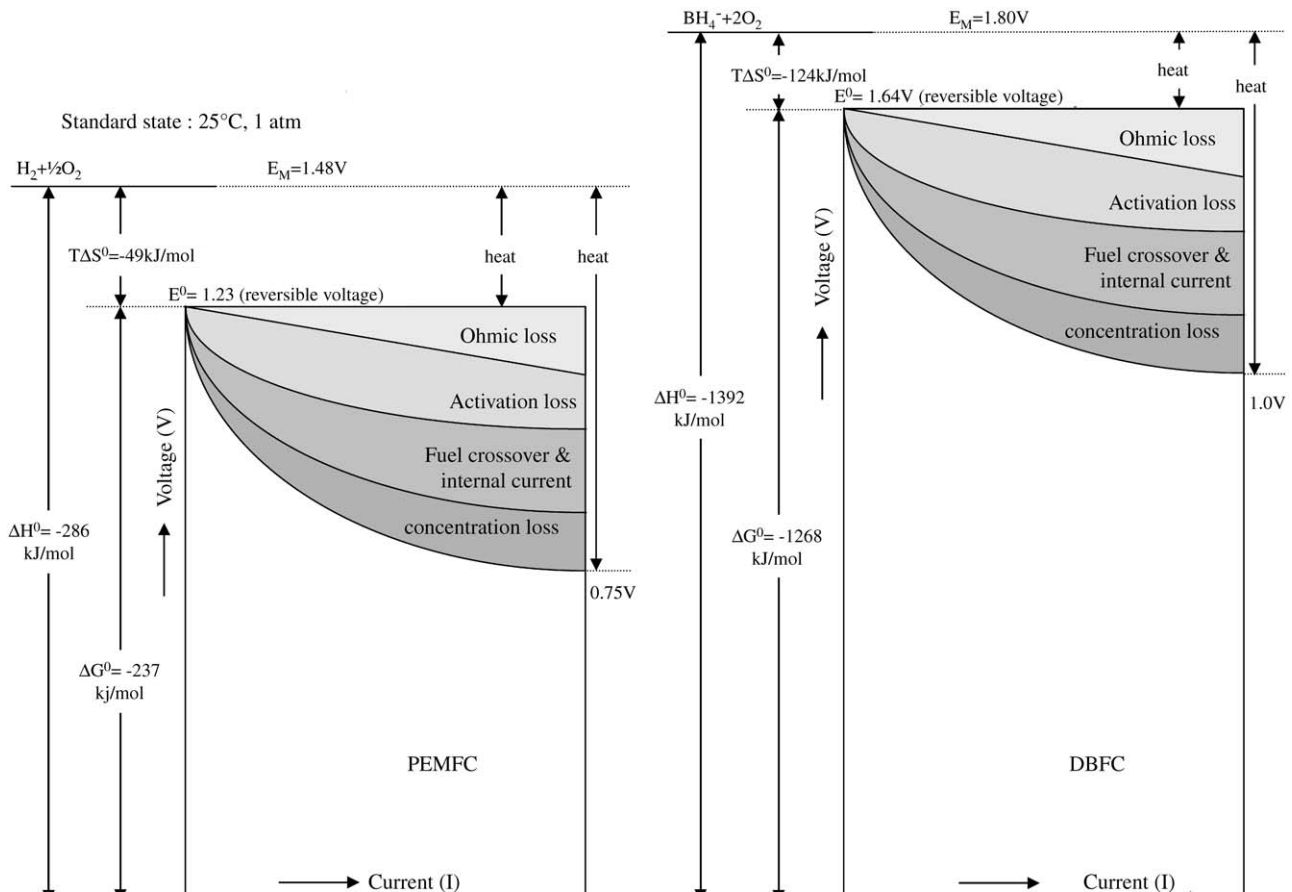


Fig. 2. Schematic performance curves of the PEMFC and the DBFC.

are the same though the applied electrolytes were different (KOH or anion exchange membrane). Model 3 is different from the models above in the charge carrier and ion migration direction.

### 3. Recent achievements

The DBFC performance depends on the MEA structure, fuel composition and operation conditions. Recently, we constructed fuel cells using a mixture of surface treated Zr–Ni Laves phase alloy  $AB_2$  ( $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ ) and Pd/C as the anode catalyst, carbon-supported Pt as the cathode catalyst and the  $Na^+$  form Nafion membrane (NRE-211) as the electrolyte. A power density  $290 \text{ mW/cm}^2$  of the cell with an air cathode has been achieved at  $60^\circ\text{C}$ . A five-cell stack with effective area of  $67 \text{ cm}^2$  demonstrated that the

power reached to  $110 \text{ W}$  when the stack temperature reached to  $60^\circ\text{C}$ , even if the stack started at room temperature without air humidification. The performances of single-cell and five-cell stack are shown in Fig. 3.

Sodium borohydride utilization depends on the applied anode catalysts,  $NaBH_4$  concentration and operation temperature. When the DBFC was operated under  $50^\circ\text{C}$ , the  $NaBH_4$  utilization reached 62% if using the fuel containing 5 wt% of  $NaBH_4$ . However, when the operation temperature was raised to  $60^\circ\text{C}$ , the  $NaBH_4$  utilization decreased to 51% as shown in Fig. 4.

### 4. Problems in research and development

Theoretically, one ion of  $BH_4^-$  can generate eight electrons, however, the number of electrons utilized per ion of

Table 1  
Classification and characteristics of the DBFCs

	Electrolyte	Charge carrier (ion migration)	Product at anode	Product at cathode
Model 1 [10]	Alkali	$OH^-$ (C $\leftarrow$ A)	$B(OH)_4^-$ , $H_2O$	–
Model 2 [4]	Anion exchange membrane (AEM)	$OH^-$ (C $\leftarrow$ A)	$B(OH)_4^-$ , $H_2O$	–
Model 3 [13]	Cation exchange membrane (CEM)	$Na^+$ (A $\leftarrow$ C)	$B(OH)_4^-$ , $H_2O$	NaOH

C: cathode; A: anode.

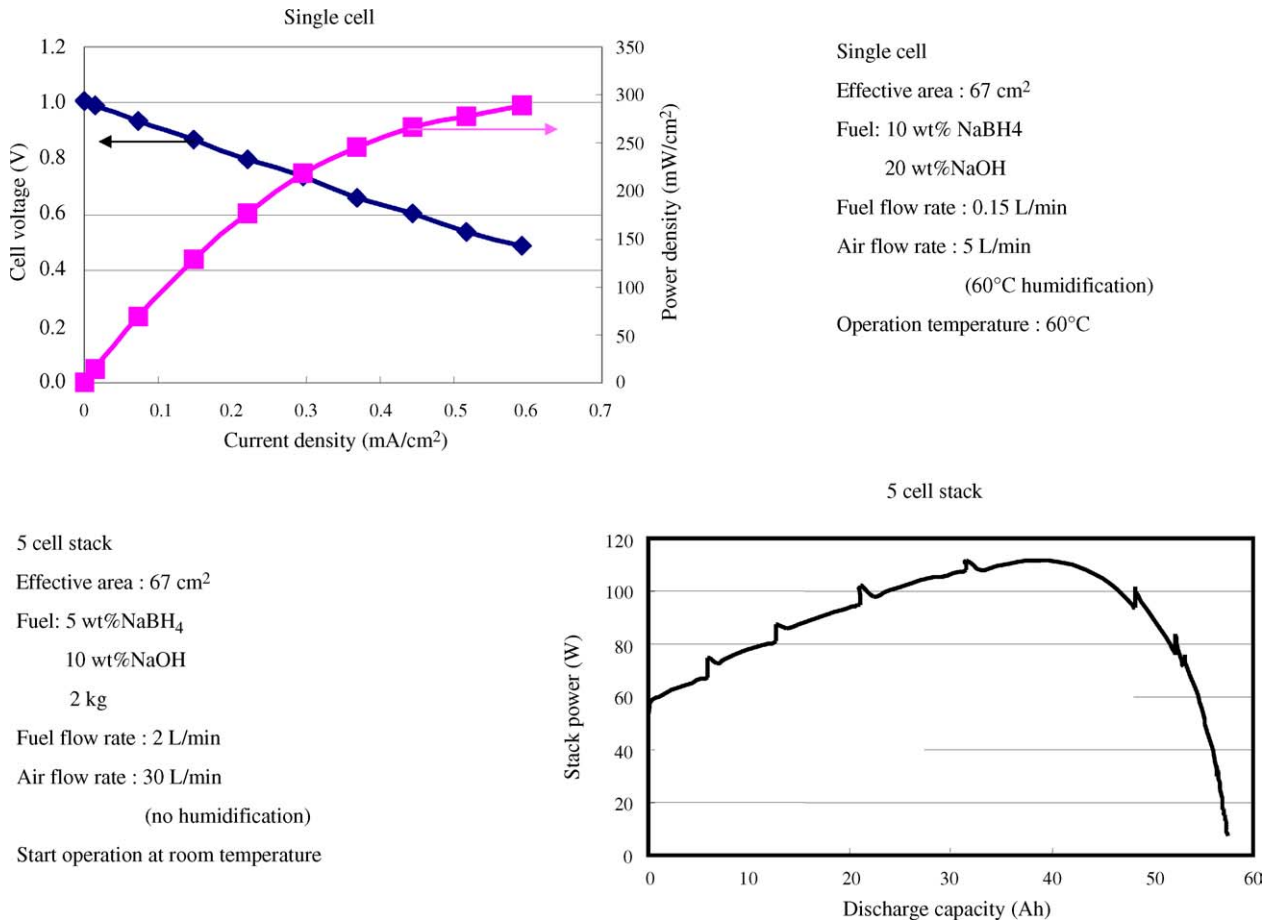
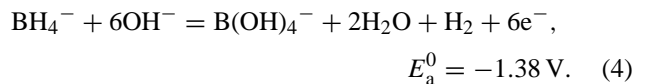


Fig. 3. Single-cell and five-cell stack performances of the DBFC.

BH<sub>4</sub><sup>-</sup> oxidized is less than eight electrons due to the applied anode catalysts. It is reported that one ion of BH<sub>4</sub><sup>-</sup> generates 6.9 electrons by using Au catalyst [3], 6 electrons by using Pd catalyst [17] and 4 electrons by using Ni catalyst [15].

In the case of using Pd as the anode catalyst, the six-electron anode reaction and standard electrode potentials

(according to the thermodynamic calculation) are shown as following:



In the case of using Ni as the anode catalyst, the four-electron anode reaction and standard electrode potentials are

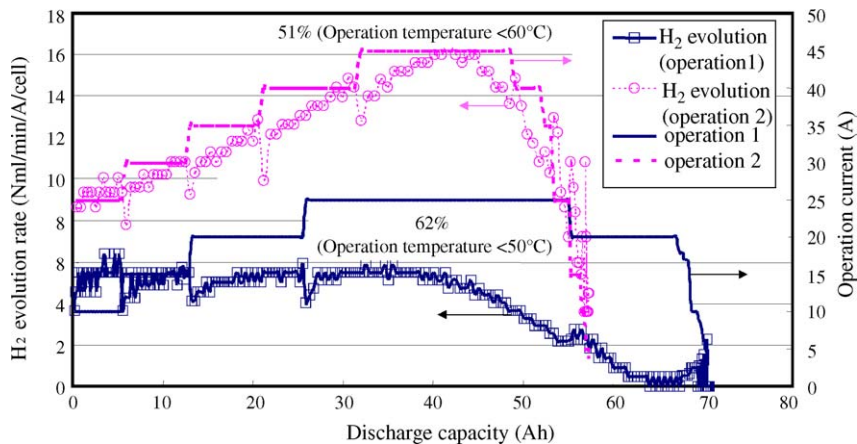
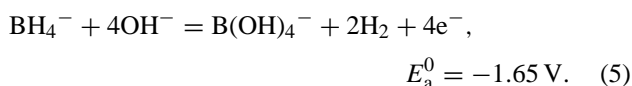
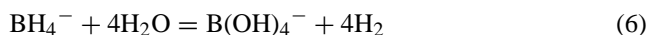


Fig. 4. Fuel utilization of the DBFC through controlling the operation temperature by changing operation pattern.

shown as following:



When electrons utilized per ion of  $\text{BH}_4^-$  decrease to 6 and 4, the electromotive force increases to 1.78 and 2.05 V, respectively. However, the generated electricity will be decreased. For example, the energy density of sodium borohydride can reach 9.3 Wh/g of  $\text{NaBH}_4$  in eight-electron reaction, however, only 7.6 Wh/g for six-electron reaction and 5.8 Wh/g for four-electron reaction can be obtained. Moreover, the by-reaction (the hydrolysis reaction of the borohydride as shown in reaction (6)) during operation is another problem that also decreases the fuel utilization.



How to restrain the borohydride hydrolysis and how to obtain eight-electron reaction are the key points to improve the columbic efficiency of the DBFCs.  $\text{NaBH}_4$  concentration in the fuel is a factor to the hydrogen evolution. It was reported that when  $\text{NaBH}_4$  concentration was less than 1.5 M,  $\text{BH}_4^-$  ion was electrochemically oxidized by an eight-electron reaction, but when the  $\text{NaBH}_4$  concentration increased to 2 M, the anodic reaction was shifted to a six-electron reaction if using Pt/C as the anode catalyst [18]. Using materials with high hydrogen over-potential and surface treatment technology are considered to be the way to restrain the hydrogen evolution. Using the evolved hydrogen to supply for the AFC or the PEMFC is another way to increase the fuel utilization from an engineering consideration.

Another problem is the cost of the fuel, sodium borohydride costs US\$ 55  $\text{kg}^{-1}$ . The fuel contribution to cost of electricity (COE) for the DBFC will be US\$ 9.7  $\text{kWh}^{-1}$  even if the operation voltage of the DBFC can reach to 1.0 V. It is 100 times compared with hydrogen gas. At present, it is very difficult to apply the DBFC to the high power applications such as car and home power generator. However, it is very possible to substitute batteries in low power applications such as primary batteries, secondary batteries for note computer, cordless electric tools, etc. because the COE for batteries is rather high. For example, the COE for alkaline primary battery will reach to US\$ 450  $\text{kWh}^{-1}$ .

## 5. Remarks

Through 4 years research and development of the DBFC, a maximum power density of 290  $\text{mW/cm}^2$  has been achieved.

The DBFC is competitive with the PEMFC in the cell performance. According to the PEMFC development history, it is no doubt that the DBFC power density can reach up to 500  $\text{mW/cm}^2$  within several years. In order to achieve this target, further efforts are needed in development of membrane-electrode-assembly constitution and structure.

For practical uses, the problem of hydrogen evolution during operation should be solved because the hydrogen evolution not only decrease the fuel utilization but also is a troublesome issue in system design.

In order to expand the application area for the DBFC, the cost reduction of the borohydride production is necessary. If the cost of borohydride production can be reduced to US\$ 0.55  $\text{kg}^{-1}$ , the DBFC will be a powerful competitor in the vehicle applications of fuel cell. Recently, there are several publications related to the new processes of borohydride synthesis [14,19–21]. We expect that a breakthrough can be achieved in reducing borohydride production cost.

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