Review

Current status and progress of direct borohydride fuel cell technology development

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ABSTRACT

In this review article, recent advances in the development of the direct borohydride fuel cell (DBFC) technology are reviewed. Based on the reported results, it is concluded that the BH_4^- electro-oxidation is determined by the catalyst used and BH_4^- concentration at the catalytic sites. Hydrogen evolution during the DBFC operation can be suppressed by: (1) using a composite catalyst or a hydrogen storage alloy as the anode catalyst via a quasi 8-electron reaction; (2) using metals with high hydrogen over-potential, such as Au and Ag as the anode catalyst via an intrinsic 8-electron reaction; and/or (3) modifying and optimizing fuel composition.

The single cell and stack performance of DBFC is mainly influenced by the hydrogen evolution, the BH_4^- cross-over, and the BH_4^- tolerance of cathode catalyst. The development of non-platinum cathode catalysts and stacking technology is on the way. The reported results are encouraging but some problems still remain to be further investigated and solved.

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Contents

1. Introduction

A new hydrogen energy conversion technology based on sodium borohydride ($NaBH_4$) has emerged in the past few years. $NaBH_4$ is a well-known chemical reducing agent. As a hydrogen storage material, it has attracted a lot of attention due to its higher gravimetric hydrogen capacity compared to metal hydrides and higher volumetric hydrogen capacity than compressed and liquefied hydrogen. Borohydride can be directly used as an anode fuel to power the direct borohydride fuel cell (DBFC) to provide a higher electrochemical potential and reactivity compared with use of gaseous hydrogen as the fuel. $NaBH_4$ is stable in dry air, and could be easily handled like common chemicals compared to many other hydrogen storage methods.

In principle, the DBFC can only work in an alkaline environment because BH_4^- is unstable in neutral or acidic medium. Electrocatalysts for both anode and cathode in DBFC with alkaline fuel are not necessarily limited to noble metals. Low cost catalysts can be expected to result in good performance. Ni-coated steels can be used to make bipolar plates so that their manufacturing cost can be greatly reduced by using simple forming techniques, such as cold pressing. Because the fuel used in the DBFC is an aqueous solution that can also act as cooling medium, the cooling plates that are included in the stacks of the proton exchange membrane fuel cell (PEMFC), are not necessary. In view of these advantages, the DBFC is considered to

Nomenclature

AEM   anion exchange membrane
CEM   cation exchange membrane
Co-PPY-C composite of cobalt-polypyrrole-carbon
CoPc   Co phthalocyanine
DBFC   direct borohydride fuel cell
DHFC   direct hydrazine fuel cell
DMFC   direct methanol fuel cell
ETFE   ethylenetetrafluoroethylene
ETFE-g-PSSA ETFE grafted with PSSA
HAP   hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)
M   hydrogen storage alloy
ORR   oxygen reduction reaction
PEMFC   proton exchange membrane fuel cell
PSSA   polystyrene sulfonic acid
PVA   poly vinyl alcohol
TU   thiourea
U_1 H_2 evolution rate from BH_4^- hydrolysis
U_2 H_2 evolution rate due to BH_4^- electro-oxidation
**U_3** H_2 consumption rate due to H_2 electro-oxidation

be a potential power supplier in mobile and portable applications.

Pecsok [1] first suggested use of alkaline borohydride solutions as the fuel in 1953. In the early development of the DBFC, many researchers were focused on the investigation of anodic reaction mechanisms and the development of anodic catalyst. By the end of the last century, Amendola and co-workers [2] constructed a borohydride/air cell using anion exchange membrane (AEM) as the electrolyte. It was reported that specific energy>180 Wh kg^{-1}, power densities >20 mW cm^{-2} at room temperature and >60 mW cm^{-2} at 70 °C were achieved. Since then, many research achievements have been reported. Li [3] and Demirci [4] summarized the merits of the DBFC in comparison to the PEMFC and the direct methanol fuel cell (DMFC). Verma and Basu [5] compared several direct alkaline fuel cells using methanol, alcohol, or NaBH$_4$ solution as the fuel. Their results showed that the fuel cell using BH_4^- solution as the fuel demonstrated the highest performance among the three. Leon [6] and Wee [7] reviewed the progresses in the development of the DBFC technology before 2006.

In this review, the anodic reaction routes of BH_4^- on some typical catalysts are summarized. Recent progress in the design of cell configuration, the development of electrode catalysts and membranes, and the development of stacking technology is reviewed. The critical issues for the DBFC technology have been highlighted and discussed.

2. Anode

Pecsok [1] and Stockmayer [8] suggested that the anodic reaction of borohydrides was as follows:
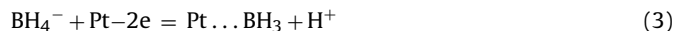
$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e^- \quad -1.24\,V(vs.SHE) \tag{1}$$
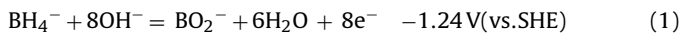
Indig and Snyder [9] investigated the polarization of the BH_4^- on Ni catalyst. They found that it was impossible to obtain the 8-electron oxidation on Ni catalyst. The electro-oxidation of BH_4^- on Ni catalyst should be described as:

$$BH_4^- + 4OH^- = BO_2^- + 2H_2 + 2H_2O + 4e^- \tag{2}$$
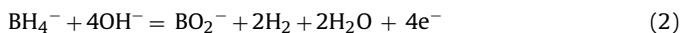
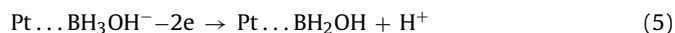Since then, it had been found that BH_4^- demonstrated interesting electro-oxidation behavior on different catalysts under different concentrations of NaBH$_4$ and NaOH [2,10–30].

Elder and Hickling [11] studied the anodic behavior of BH_4^- on a smooth platinum electrode in details. They proposed a reaction scheme as follows:

Initial step:

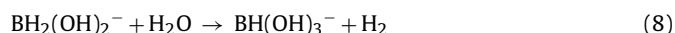$$BH_4^- + Pt - 2e = Pt \ldots BH_3 + H^+ \tag{3}$$

$$Pt \ldots BH_3 + OH^- \rightarrow Pt \ldots BH_3OH^- \tag{4}$$

Rate-determining step:

$$Pt \ldots BH_3OH^- - 2e \rightarrow Pt \ldots BH_2OH + H^+ \tag{5}$$

$$Pt \ldots BH_2OH + H_2O \rightarrow Pt + BH_2(OH)_2^- + H^+ \tag{6}$$

Slow hydrolysis:

$$Pt \ldots BH_3OH^- + H_2O \rightarrow Pt + BH_2(OH)_2^- + H_2 \tag{7}$$

Completion step:

$$BH_2(OH)_2^- + H_2O \rightarrow BH(OH)_3^- + H_2 \tag{8}$$

$$BH(OH)_3^- \rightarrow H_2BO_3^- + H_2 \tag{9}$$

The overall reaction gave a coulombic number between 2 and 4 for each BH_4^- ion.

Unlike Pt, electrode materials such as Au and Ag showed little or no activity towards the BH_4^- hydrolysis reaction. As a consequence, the coulombic numbers near 8 were reported for the electro-oxidation reaction of BH_4^- [2,27,28]. But these electrode materials usually demonstrated slow electrode kinetics and low power density. Gyenge and co-workers suggested that alloying Ag with Ir and Pt could effectively improve the electrode kinetics [87].

Lee and co-workers [24] suggested a quasi 8-electron reaction route by which hydrogen storage alloy ($ZrCr_{0.8}Ni_{1.2}$) absorbed hydrogen from a borohydride solution, and then the hydrogen was electrochemically oxidized to generate electricity. It was reported that the higher fuel utilization efficiency was achieved, as shown in Fig. 1, as a result of full hydrogen transfer from borohydride to the hydrogen storage alloy, which was then totally eletro-oxidized through the following reaction:

$$MH_x + xOH^- = M + xH_2O + xe^- \tag{10}$$

M stands for a hydrogen storage alloy. Wang and co-workers [25] also reported that the fuel utilization efficiency could reach up to 90% when AB$_5$ type alloy LaNi$_{4.5}$Al$_{0.5}$ was used as the anode catalyst.

Liu and co-workers [26] studied the difference between the BH_4^- electro-oxidation on Ni and hydrogen storage alloy. It was
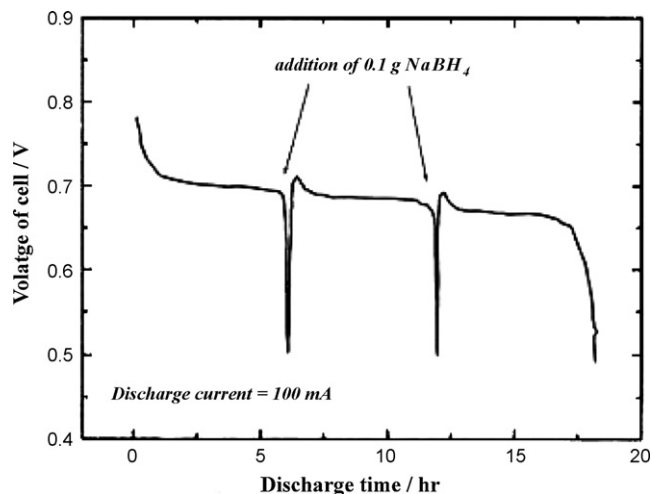

Fig. 1. A current discharge curve of a fuel cell containing BH_4^- [24].
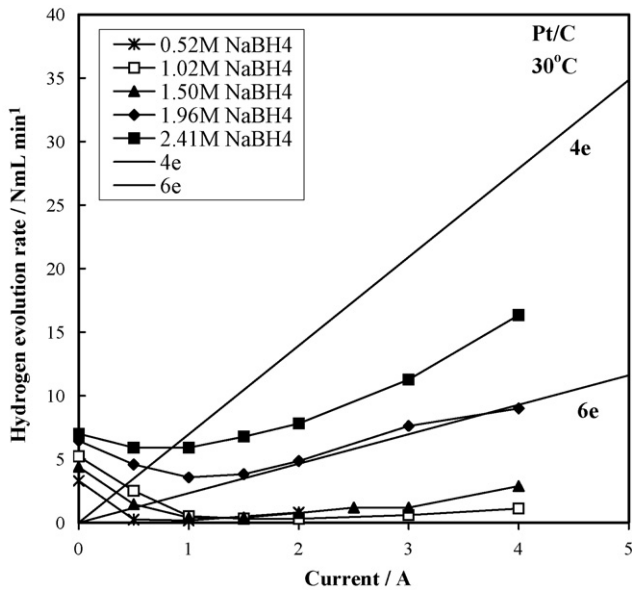
Fig. 2. Relation of the hydrogen evolution rate with the anode current at different borohydride concentrations for the Pt/C electrode [27].

reported that the open-circuit potential of BH_4^- on Ni-based hydrogen storage alloys was less negative than that on the pure nickel electrode. It was found that the electrochemical oxidation of atomic hydrogen in hydrogen storage alloys was kinetically favorable only at low borohydride concentrations and low temperatures. It was reported that higher coulombic number could be achieved at Pt/C electrode when using borohydride solutions with relatively low concentrations as shown in Fig. 2 [27]. Li and co-workers [31] suggested that coating a thin Nafion film on the Pd/C reduced BH_4^- concentration at the catalytic sites. It was reported that Nafion addition to the anode could effectively suppress hydrogen evolution by a decrease of the isolated catalysts and a regulation of the borohydride concentration on the catalyst surfaces as shown in Fig. 3.

Li and co-workers [27,31] noted the fact that by increasing the operational current of the cell, a minimum value of hydrogen evolution took place when BH_4^- was electro-oxidized on carbon supported Pt and Pd. They summarized the hydrogen evolution behavior during the DBFC operation as shown in Fig. 4. Generally, during a DBFC operation, gaseous hydrogen was produced from the borohydride hydrolysis on the isolated catalyst particles by the following reaction:
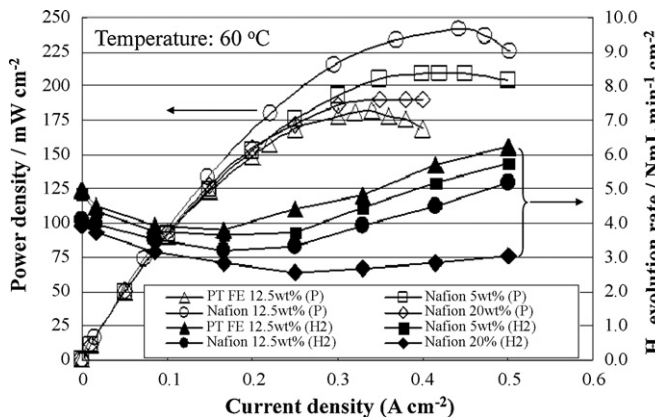
$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \tag{11}$$

Fig. 3. Nafion addition effects on H_2 evolution depression and cell performance [31].
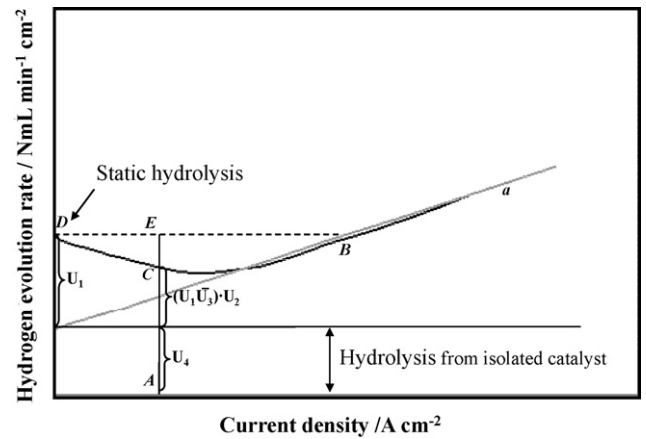
Fig. 4. Schematic hydrogen evolution behavior during operation of the DBFC [31]. $(\mathbf{U_1}\bar{\mathbf{U}}_3)\cdot\mathbf{U_2}$ is a logic function. $\mathbf{U_1}$: H_2 evolution rate from BH_4^- hydrolysis; $\mathbf{U_2}$: H_2 evolution rate due to BH_4^- electro-oxidation; $\mathbf{U_3}$: H_2 consumption rate due to H_2 electro-oxidation.

Hydrogen was also produced by the following anodic reaction of the borohydride:

$$BH_4^- + xOH^- = BO_2^- + (x-2)H_2O + (4-0.5x)H_2 + xe^- \tag{12}$$
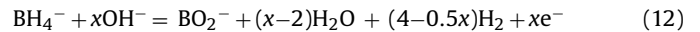
There were three competitive reactions occurring on the catalyst sites:

(1) borohydride hydrolysis reaction,
(2) borohydride electro-oxidation reaction, and
(3) hydrogen electro-oxidation reaction.

It was considered that BH_4^- would be electro-oxidized via a quasi 8-electron reaction on the carbon-supported Pt electrode when using dilute BH_4^- solution as the anolyte while operating cell at high currents [27]. Almost a cessation of hydrogen evolution was found. Similar phenomenon was observed when using carbon-supported Pd (Pd/C) as the anodic catalyst. It was also found that a 4-electron reaction occurred on Pd/C catalyst when using concentrated $NaBH_4$ solutions as the fuel, but as noted above, a higher coulombic efficiency could be achieved at relatively low borohydride concentrations and large anode currents.

Fuel composition modification was considered to be another way to suppress hydrogen evolution during operation. Gyenge [32,33,86] suggested adding thiourea (TU) or tetraethylammonium hydroxide into anolyte to depress the borohydride hydrolysis. However, the thiourea could not change the borohydride electro-oxidation behavior on Pt. Martins et al. [34] studied the electrochemical behavior of BH_4^- on a Pt electrode in the absence and presence of TU by cyclic voltammetry. It was found that TU addition (concentration ratio of TU/$NaBH_4$: 0.6/1) inhibited the hydrolysis of BH_4^-. The BH_4^- could be electro-oxidized on Au catalyst by an 8-electron reaction (Fig. 5).

It was considered that hydrazine (N_2H_4) was alkalescent and could stabilize the borohydride ions. Furthermore, N_2H_4 itself could also be used as a fuel in the direct hydrazine fuel cell (DHFC) [35]. Li and co-workers suggested that adding N_2H_4 to the alkaline borohydride solutions could suppress the gas evolution of the DBFC [36]. It was reported that BH_4^- would be mainly oxidized on Pd whereas N_2H_4 would be mainly oxidized on Ni or surface-treated Zr-Ni alloy catalyst when using alkaline $NaBH_4$-N_2H_4 solutions as the fuel and a composite of Pd, Ni, and surface-treated Zr-Ni alloy as the anodic catalyst. The DBFC performance was improved by adding N_2H_4 into the alkaline $NaBH_4$ solutions.

From these reported results, it can be concluded that the BH_4^- electro-oxidation is determined by the applied catalyst and BH_4^-

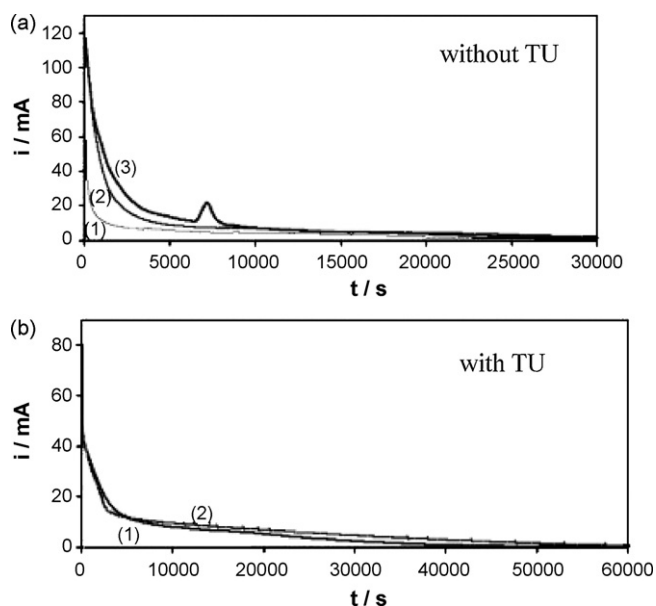**Fig. 5.** Comparison of discharge curves of BH_4^- with and without TU [34].

Fig. 6. Single cell performances of the DBFC uisng CEM [3].

concentration on the catalytic sites. Hydrogen evolution during a cell operation can be suppressed by:

(1) using a composite catalyst or hydrogen storage alloy as the anode catalyst via a quasi 8-electron reaction,
(2) using metal with high hydrogen over-potential, such as Au and Ag as the anode catalyst via an intrinsic 8-electron reaction, and/or
(3) modifying fuel composition.

3. Cathode

Since the end of the last century, many investigations on anode catalysts of the DBFC were carried out using Pt as the cathode catalyst. Recently, the development of cathode catalyst other than platinum has received much attention. It was reported that Ag [28,37] and MnO_2 [20,38,39] exhibited good initial performance reaching as close as the performance of Pt. Chatenet et al. [39] studied the selectivity of oxygen reduction reaction on various carbon-supported catalysts, such as Pt/C, Au/C, Ag/C, MnO_x/C, and MnO_x–Mg/C in NaOH solution with the presence of BH_4^-. It was found that there was a competition between the oxygen reduction reaction (ORR) and the BH_4^- hydrolysis and/or oxidation. Manganese oxide-based electrocatalysts demonstrated very good ORR activity even if traces of BH_4^- existed. Basu and co-workers [40] studied the effect of MnO_2 loading amount on the cell performance. It was found that the power density of the fuel cell increased with the increase of MnO_2 loading to a certain limit but then decreased with further loading. The maximum power density was obtained at MnO_2 loading of $3\,mg\,cm^{-2}$.

It was known that the transition metal (e.g. Fe, Co) macrocyclic compounds (e.g. porphyrins, phthalocyanines, tetraazannulenes) could be used as electrocatalysts for oxygen reduction in alkaline fuel cell after Jasinski's discovery of the catalytic properties of Co phthalocyanine (CoPc) [41]. It was also found the catalytic activity of Co phthalocyanine was comparable to that of Pt and Ag [42]. Transition metal macrocyclic compounds could function as a cathode catalyst of the DBFC similar to that of Pt. It was reported that Fe or Co tetramethoxyphenyl porphyrin [43], metal phthalocyanines [44,45] and cobalt polypyrrole carbon composite (Co-PPY-C) [46] also demonstrated good cell performances and excellent BH_4^- tol-
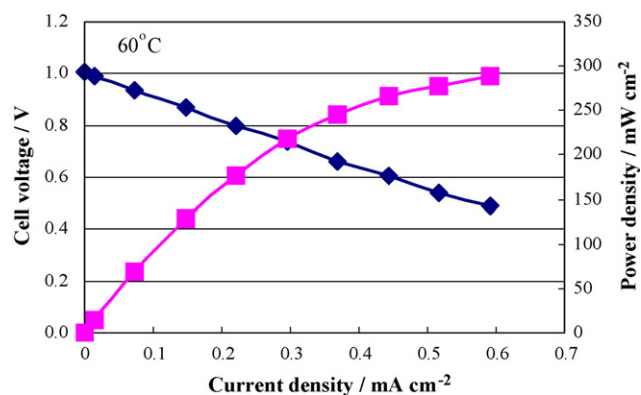
erance. However, the detailed mechanism of their performance is not clear.

4. Electrolyte

In the early development of the DBFC, alkaline solutions were used as the electrolyte [47]. However, more recently, ion exchange membranes, such as cation exchange membrane (CEM) and anion exchange membrane (AEM) were used as the electrolyte. Considering that BH_4^- was an anion, it was considered that CEM was more effective in the suppression of BH_4^- cross-over than AEM. Nafion membranes were thus considered to be a good electrolyte in the DBFC [48], and peak power density of $290\,mW\,cm^{-2}$ was achieved at $60\,°C$ as shown in Fig. 6 [3]. At ambient and passive conditions, the maximum power density reached up to $80\,mW\,cm^{-2}$ [49]. Lakeman [50] and Cheng [51] confirmed that Nafion membranes could be used as an electrolyte to separate anolyte from cathode. It was reported that the cell performance was dependent upon the thickness of the applied Nafion membranes [30].

The DBFCs using a poly (vinyl alcohol)/hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (PVA/HAP) composite polymer membrane were suggested by Yang et al. [52]. The peak power density of ca. $45\,mW\,cm^{-2}$ was achieved at ambient conditions. Cheng et al. [53] prepared and evaluated several radiation grafted ion exchange membranes. It was reported that the performance of a DBFC using ETFE-g-PSSA membrane was higher than that of a DBFC using Nafion 117 membrane as shown in Fig. 7. The peak power density reached up to $112\,mW\,cm^{-2}$ at $85\,°C$. The ETFE-g-PSSA membrane was fabricated by grafting styrene onto polyethylenetetrafluoroethylene (ETFE) followed by a subsequent sulphonation reaction. The ETFE-g-PSSA stands for polyethylenetetrafluoroethylene-g-polystyrene sulfonic acid.

Scott and co-workers [54] constructed a DBFC using an anion exchange membrane, a Pt–Ru/C anode, and a Pt/C cathode. The effects of oxidant (air or oxygen), borohydride and NaOH concentrations, and operation temperature as well as anode solution flow rate were extensively investigated. The DBFC gave power densities of 200 and $145\,mW\,cm^{-2}$ using ambient oxygen and air as oxidants, respectively, at medium temperatures ($60\,°C$). The performance of the DBFC was very good at low temperatures (ca. $30\,°C$).

Ma et al. [44,45] suggested a simple, highly efficient, and low-cost DBFC without using ion exchange membranes. It was found that CoPc not only exhibited considerable electro-catalytic activity for ORR in the BH_4^- solutions, but also found that the existence of BH_4^- ions had negligible influence on the discharge performances of the air-breathing cathode. A maximum power density of 90 mW cm^{-2} was obtained at a current density of $175\,mA\,cm^{-2}$ at ambient conditions.
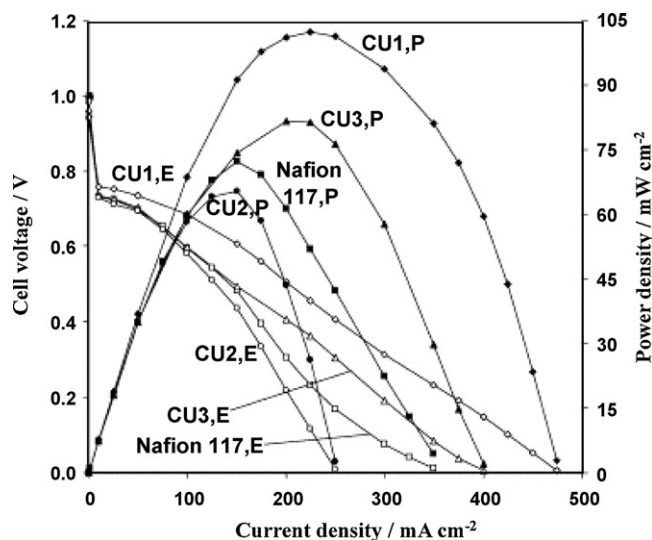
Fig. 7. Steady cell voltage (E) and power density (P)–current density curves collected from the DBFC with developed membranes and Nafion® 117 membranes [53].

Fig. 8. Current–voltage curves for anode diffusion layers with various thicknesses [56].

5. Cell and stack performance

Choosing metal with high electro-catalytic activity as the electrode catalyst was a conventional way to improve the cell performance. Lee and co-workers [29] assembled the DBFCs using carbon supported Pt or unsupported Pt catalyst. It was reported that the maximum power density only could reach to 44.2 mW cm^{-2}. Gyenge et al. [55] reported that Pt-Ni and Pt-Ir exhibited higher electro-catalytic activity than Pt giving a cell voltage of 0.53 V at 100 mA cm^{-2}. However, the maximum power density around 50 mW cm^{-2} was still lower than that of the PEMFC. It was considered that the electro-catalytic activity of applied anode catalyst was not the sole critical issue to the DBFC performance improvement. Li and co-workers [30,31] studied the influence of hydrogen evolution on the cell performance. They found that reduction of the effective reaction area caused by hydrogen evolution during the DBFC operation was a more critical problem [30]. They suggested that addition of Nafion in anode and using a composite of Ni, MH, and Pd/C as the anode catalyst improved the cell and stack performance of the DBFC by suppressing the hydrogen evolution [30,31].

Suppression of hydrogen evolution during operation was one of the solutions to improve cell performance. On the other hand, how to reduce the influence of hydrogen evolution on the decrease of effective reaction area was another way to improve cell performance. Through anolyte flow observation in a transparent cell, Park [56] and Liu [30] confirmed that hydrogen bubbles blocked channels and thus hindered the anolyte flow. Park et al. [56] investigated the effect of the anode diffusion layer on the cell performance and stability of the DBFC. It was found that the thinner the anode diffusion layer, the higher performance was obtained, as shown in the Fig. 8. Liu et al. [30] tried to increase anode porosity by pasting anode ink into a piece of Ni-foam. It was found the cell performance was improved from 50 to 180 mW cm^{-2} [30]. Ha and co-workers tried to improve the stack performance by decrease of hydrogen evolution influence through suitable anode shape design [57] and the flow field improvement [58].

Li and co-workers constructed a series DBFC stack by using inner [3,30] and external [59] fuel manifolds. It was found that the hydrogen evolution was one of the most critical problems that influence the DBFC stack performance [30]. The hydrogen evolution resulted in an uneven fuel distribution between the cells of the stack. The influence of the hydrogen evolution on the stack per-
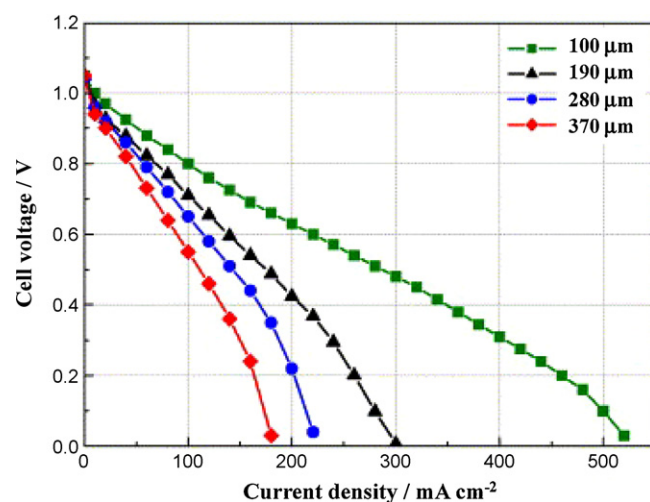
formance could be reduced by changing the fuel supply pattern in the stack. Considering that the alkaline sodium borohydride solution was conductive, Luo et al. [60] pointed out that the alkaline BH$_4^-$ solution might result in short circuiting the neighboring cells with traditional integrated fuel manifolds if the bipolar stack was not properly designed and engineered. Perhaps it would be another factor that influence the DBFC stack performance after solving the hydrogen evolution problem.

After exploring the possibility of DBFC operating under ambient and passive conditions [61], Liu et al. constructed 2-cell and 8-cell planar DBFC modules for portable applications [49]. By using Ni-Pd/C composite as the anode catalyst and Nafion as the binder, a peak power density of 75 mW cm^{-2} was achieved by the 2-cell module, and a stable power output of 2.5 W was obtained by the 8-cell module with a compact structure (electrode area: 6 cm^2).

According to the Nernst equation, it was known that high concentration of BH$_4^-$ was good for the cell performance. However, it was found that the increase of NaBH$_4$ concentration improved the anode performance a little but resulted in an obvious increase in the cathode polarization when using highly concentrated BH$_4^-$ solutions as the fuel [62]. Hence, the cross-over of BH$_4^-$ was considered to be another critical issue to influence the cathode performance [37]. It was found that the applied current during the cell operation would influence the fuel cross-over, possibly due to a decrease of the fuel concentration gradient across the membrane caused by fuel depletion around the anode. The Pt cathodes were found to have better performance stability than the Ag cathodes. The cell stability within hours was found to be greatly affected by the mass transport properties of different components. The porosities of the anode and cathode supporting materials, the membrane pretreatment, and borohydride concentration had significant influence on the performance stability [63].

Cheng et al. [64] considered that electric conductivity of anode was another factor to influence the cell performance. They suggested the use of titanium mesh-supported gold and silver anodes, and found that the mesh anodes gave higher current densities and higher cell power densities than those obtained with carbon-supported anodes.

Based on these reported results, it can be concluded that the cell and stack performances of the DBFC are mainly influenced by the hydrogen evolution, the BH$_4^-$ cross-over, and the BH$_4^-$ tolerance of the cathode catalyst. Hydrogen evolution results in the decrease of effective reaction area during operation. BH$_4^-$ cross-over from anolyte to cathode side results in a mixed potential of the cath-

ode. Improvement of BH_4^- tolerance of the cathode catalyst would lessen the influence of BH_4^- cross-over.

6. DBFCs using H_2O_2 as the oxidant

Choudhury et al. [65] suggested a DBFC using hydrogen peroxide (H_2O_2) as oxidant. As pointed out by Raman [66], the unique combination of $NaBH_4$ and H_2O_2, both of which were used in aqueous form, gave a possibility to design a unitized refueling system that was inherently compact compared to fuel cells that used gaseous reactants. Such a fuel cell was expected to be used in submersible and cosmic applications.

Miley et al. [67] studied watt-level prototype cells and confirmed the feasibility and excellent performance of the DBFC using H_2O_2 as the oxidation agent. Parametric system analyses were carried out to study the feasibility of 500 W and 5-kW units for future Lunar and Mars missions. Experiments demonstrated that the direct utilization of H_2O_2 and $NaBH_4$ at the electrodes resulted in more than 30% higher voltage output compared to the ordinary H_2/O_2 fuel cell.

Raman [66,68] suggested using Nafion (R)-961 membrane as electrolyte to separate anolyte from catholyte. It was found that the use of a Nafion (R)-961 membrane lessened the cross-over of BH_4^- from the anode to cathode. A 28-W BH_4^-/H_2O_2 fuel-cell stack operating at 25 °C was reported for contemporary portable applications. The peak power density of ca. 50 mW cm^{-2} was achieved. This performance was superior to the anticipated power-density of 9 mW cm^{-2} for a methanol-hydrogen peroxide fuel cell.

Miley and co-workers [69] suggested electro-deposition and plasma sputtering deposition methods to prepare anode and cathode. A peak power density of ca. 600 mW cm^{-2} was achieved at 60 °C with a direct BH_4^-/H_2O_2 fuel cell which employed palladium as the anode catalyst and gold as the cathode catalyst (Fig. 9).

7. BH_4^- in other batteries

Considering the orientation problem of the liquid fuel cell in mobile applications, Li and co-workers suggested use of alkaline $NaBH_4$ gel to power a $NaBH_4$-air battery. A peak power density of 50 mW cm^{-2} was achieved at ambient and passive conditions [70]. Hong et al. [71] suggested adding $NaBH_4$ into an alkaline electrolyte of a Zn/air or MH/air battery to improve its capacity. It was reported that an intrinsic DBFC/MH(or Zn)-MnO_2 battery could deliver a higher peak power than regular DBFCs.

Fig. 9. V–I curve and P–I curve generated by sputtered gold catalyst layer and electrodeposited palladium layer at 60 °C [69].

8. Critical problems and recommendations

Since the hydrogen evolution decreases not only the DBFC performance but also the $NaBH_4$ utilization, it is considered that the ultimate solution to hydrogen evolution is finding some anode catalysts on which BH_4^- can be completely electro-oxidized via a quasi or intrinsic 8-electron reaction and no hydrolysis reaction occurs. Complete electro-oxidation of BH_4^- via a quasi 8-electron reaction usually can be obtained when drawing large currents from the anode. This requires minimization of ohmic resistance and cathode polarization of the DBFC. Meanwhile, the fuel supply should be regulated by the power demand.

How to improve the electro-catalytic activity without decreasing the hydrogen over-potential would be a key point to the development of anode catalysts. However, it would be very difficult because the catalysts with high hydrogen over-potential usually have big anodic polarization drop when BH_4^- is electro-oxidized. Jamard et al. [72] considered that the solution to get a powerful DBFC system with high efficiency might not be to stop hydrogen evolution but preferably to run it down to keep an accurate balance between the amount of H_2 released and the amount of H_2 electro-oxidized simultaneously by the DBFC. On the other hand, more efforts should be made in optimization of the flow field design and improvement of anode structure such as forming hydrophobic pore to reduce the influence of hydrogen evolution on the effective reaction area.

The inhibition of the borohydride cross-over is another key issue in the development of the DBFC technology. However, it is very difficult to synthesize the membrane with high selectivity. Recent progress in the development of transition metal macrocyclic compounds as the cathode catalyst give some encouraging results [44,45], because the cathode catalysts with high BH_4^- tolerance can lower the influence of cross-over on the cathode polarization.

The DBFC technology has attracted more and more attention but it is still at its initial development stage. Besides the critical problems mentioned above, there are many problems to be solved such as durability of each component in the DBFC, meta-borate crystallization at anode after use, stacking loss, DBFC system design, meta-borate recycling, and so on. Though some physical and chemical properties of BH_4^- and BO_2^- solutions have been valuated [62,73,85], the obtained data are still not sufficient for the DBFC system design.

$NaBH_4$ production at low cost is the most critical issue for the application of the DBFC. Meta-borate recycling is also an important issue to reduce $NaBH_4$ production cost. Several $NaBH_4$ synthesis technologies have been developed such as ball-milling synthesis [59,74–76] and thermal synthesis [77–83]. Some electrochemical synthesis methods of BH_4^- from borate or trimethyl borate were attempted [84,85], but the results were negative. It is expected that a breakthrough can be achieved soon in reducing the borohydride production cost.

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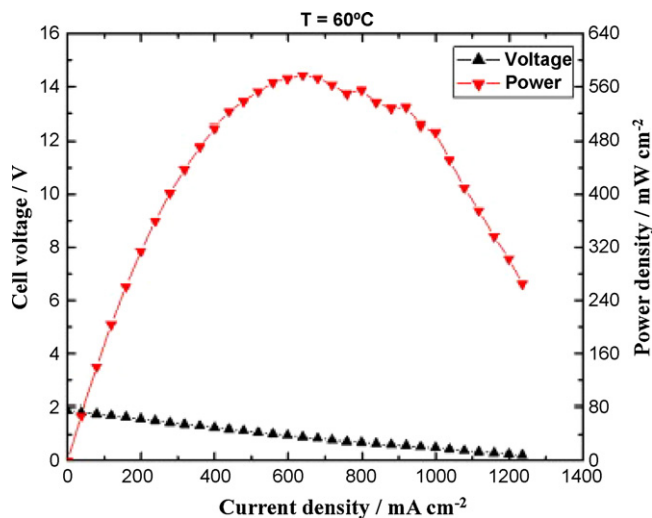[4] B. Umit, Demirci, J. Power Sources 172 (2007) 676–687.

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