

Short communication

# Development of high-performance planar borohydride fuel cell modules for portable applications

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## Abstract

Direct borohydride fuel cell (DBFC) as a liquid type fuel cell is promising for portable applications. In this study, we report our recent progress in the micro-fuel cell development. A power density of  $80 \text{ mW cm}^{-2}$  was achieved in passive mode at ambient conditions when using the anode containing nickel, carbon-supported Pd catalyst and Nafion ionomer. Current efficiency was also found to be greatly increased due to the use of Nafion rather than polytetrafluoroethylene (PTFE). Based on improvements on single cell performance, planar multi-cell power modules were assembled to study the feasibility of making high-performance and practical DBFC power units. A power of 2.5 W was achieved in a fully passive eight-cell module after significantly simplifying cell structure.

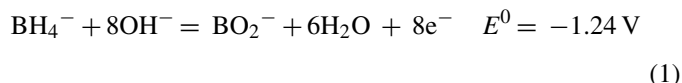
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**Keywords:** Direct borohydride fuel cell; Anode; Power; Efficiency; Power module

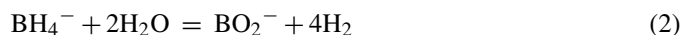
## 1. Introduction

In recent years, rapid developments of portable electronic devices demand new power sources with higher energy density than currently used Li-ion secondary battery to achieve longer operation hour and shorter recharging time. Direct methanol fuel cells (DMFC) are regarded as promising candidates for portable applications due to high energy density of methanol and easy handling of liquid fuel. However, current status of DMFC performance is still far from the requirements for commercialization. The major obstacles encountered in the development of the DMFC are the low activity of methanol and its crossover to the cathode side. The toxicity of methanol is another major concern for its commercialization. Recently, there is increasing interest on another liquid type fuel cell: the direct borohydride fuel cell (DBFC). The advantages of the DBFC include very high energy densities of borohydrides, good power performance at low temperatures, possibility of using non-noble metals as both anode and cathode electrocatalysts due to alkaline medium, and less toxicity of borohydride and its oxidation product. A brief

comparison of the DMFC and DBFC is shown in Table 1. More detailed information can be found in review papers [10,23]. The merits of DBFCs attract rapidly growing research interests both from fundamental and practical points of view [1–30]. The major research endeavors on DBFC developments focused on anode catalysts as undesirable hydrogen evolution usually occurred during borohydride oxidation. It has been shown that the electrochemical oxidation of borohydride in the flowing reaction:



is usually accompanied by a parallel hydrolysis reaction:



We have found that anode performances including current efficiency were strongly dependent on electrode material as well as borohydride concentration [12,13]. Electrocatalysts including Pt, Pd, Au, Ag, Ni, Os and some hydrogen storage alloys have been tested as anode materials for DBFC [1–9,11–18]. It was well reported that high coulombic numbers near 8e were obtained by using Au anodes due to its inactivity towards the hydrolysis reaction [1,9,15,28]. Electrochemical oxidation of borohydride ions on an Au electrode proceeds mainly through

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Table 1  
A brief comparison between DMFC and DBFC

FC	Overall reaction	Theoretical cell voltage (V)	Energy density of fuel	State-of-art power density ( $\text{mW cm}^{-2}$ )
DMFC	$\text{BH}_4^- + 2\text{O}_2 = \text{BO}_2^- + 2\text{H}_2\text{O}$	1.64	$6.1 \text{ Wh g}^{-1}$ $\text{CH}_3\text{OH}$	290 (333 K) [29]
DBFC	$\text{CH}_3\text{OH} + 3/2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$	1.21	$9.1 \text{ Wh g}^{-1}$ $\text{NaBH}_4$	80 (333 K) [23]

the direct oxidation of  $\text{BH}_4^-$ , which showed the oxidation wave at around  $-0.4 \text{ V}$  versus NHE [9,15,28], a potential much more positive than the theoretical potential. Therefore, the direct oxidation of borohydride ions on Au electrodes demonstrated high current efficiency but low voltage efficiency. On the other hand, anodic oxidation of borohydride on Ni, Pt, Pd takes place predominantly through the oxidation of hydrolysis intermediates such as  $\text{BH}_3\text{OH}^-$  or atomic hydrogen [11–13]. They showed oxidation waves at potentials more negative than that of  $\text{BH}_4^-$  [28]. Therefore, these electrodes usually show good power performance but reduced current efficiencies [13]. In both cases, there are tradeoffs between voltage and current efficiency, which is not desirable in fuel cell development. It is thus very challenging to develop anode catalysts with both high voltage and current efficiency.

In this paper we report our recent progress in development of micro-DBFC aiming for portable applications. The single cell performance including power density and current efficiency was significantly improved by using composite anode materials and Nafion ionomer as the binder. Based on the improvements on single cell, planer multi-cell modules were constructed to show the feasibility of DBFCs as practical power sources. Good performance exhibited by these DBFC power units promises their potential in practical applications.

## 2. Experimental

Anodes using composite catalysts were prepared by adding nickel powder (INCO Inc., type 210), carbon-supported palladium catalyst (10% Pd on Vulcan XC-72, E-Tek Co.), 10 wt.% Nafion solution or PTFE emulsion (60% PTFE) and de-ionized water together to form a paste and then the paste was brushed on one side of a piece of nickel foam. A typical composition was Ni:Pd/C:Nafion=0.75:0.3:0.1. The average loading of the composite material was  $20 \text{ mg cm}^{-2}$ . The electrode was then dried in air and ready for use. Cathodes were commercially available with a catalyst loading of Pt  $1 \text{ mg cm}^{-2}$  (the catalyst was Pt 30 wt.% on Vulcan XC-72). Nafion N115 or N112 membrane was used to separate fuel from the cathode and also allow ion transfer. The membrane was pretreated by boiling in 3%  $\text{H}_2\text{O}_2$  solution and de-ionized water each for 1 h successively.

The structure of single cell was described in our previous paper [6]. In short, the cell was consisted of two stainless steel endplates with slits for fuel or air. A plastic container with a volume of about 30 ml was attached to one of the plate for borohydride solution. The anode–membrane–cathode assembly was mechanically fixed in two endplates without the process of hot-pressing. The effective area of the cell was  $6 \text{ cm}^2$ .

Planar multi-cell modules were constructed to study feasibility of making practical power units. First, a two-cell module was made by putting two cells on one plane. As shown in Fig. 1, two pairs of stainless steel endplates were put in a plastic frame for mechanical integrity and electrical insulation of individual cell. The effective area of each cell was  $6 \text{ cm}^2$ . Also a fuel tank with a volume of 40 ml was attached to the two-cell unit on the anode side.

On the basis of two-cell tests, the power unit was expanded to eight cells. To make the unit lighter and more compact as well as easy for assembly, the cell structure was significantly simplified, as illustrated in Fig. 2. Endplates were replaced by Au-plated nickel mesh for current collecting and fuel or air flowing. Each MEA was sandwiched by two pieces of meshes. The center of the unit was a plastic frame with eight grids, four for each side. After the MEAs were fitted on the center frame, a space was formed for borohydride solution. The total volume of fuel was 20 ml and the final size of the module was  $7 \text{ cm} \times 9 \text{ cm} \times 2.4 \text{ cm}$ . Also each cell had an effective area of  $6 \text{ cm}^2$ .

The fuel was prepared by dissolving sodium borohydride (Finnish Chemicals, 98% purity) in 20 wt.% sodium hydroxide solution. The tests in all the research were carried out at room temperature around  $25^\circ\text{C}$  and ambient conditions. The cells were operated in a fully passive condition without any pumps and other auxiliary facilities.

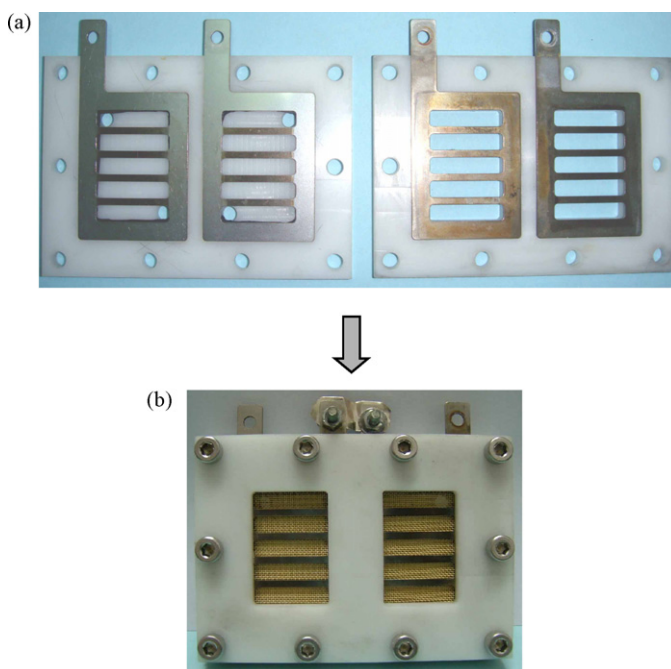


Fig. 1. Pictures of the two-cell planar module. (a) Endplates before assembling: (left) anode side and (right) cathode side. (b) After assembling.

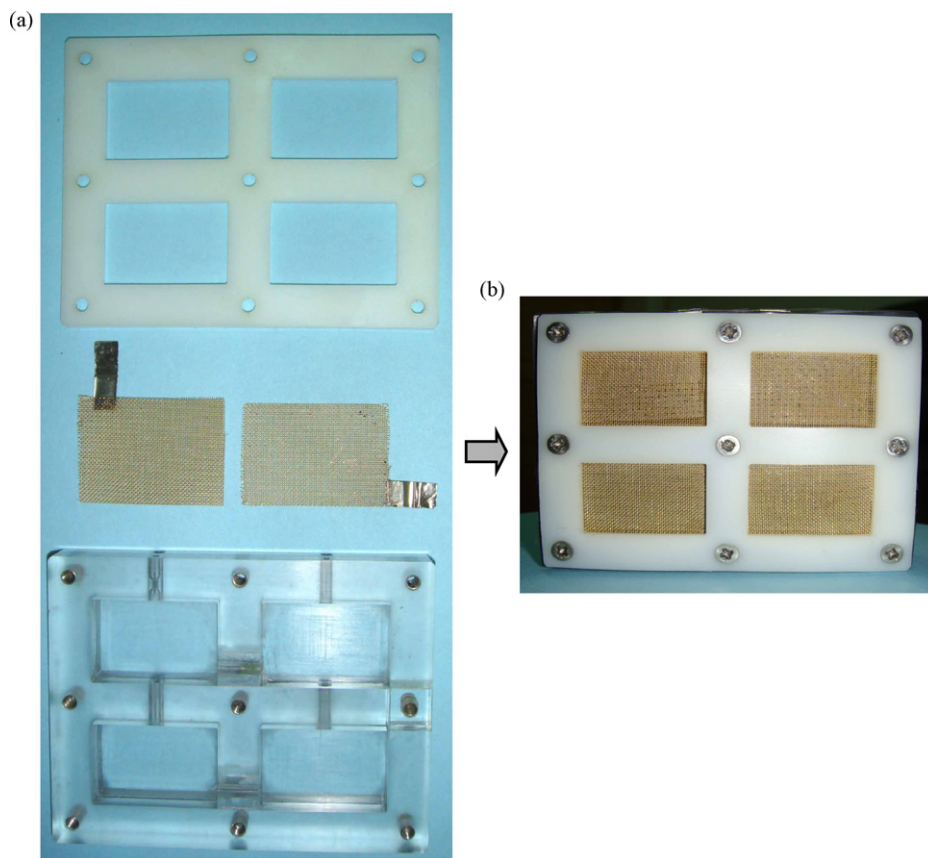


Fig. 2. Pictures of the eight-cell module before and after assembling. (a) (up) Frame of the cathode side, (middle) Au-plated Ni-meshes and (down) center frame. (b) The module after assembling.

Electrochemical impedance spectrum (EIS) analysis was carried out on a Zhaner IM6 electrochemical workstation. The spectra were recorded at open-circuit condition in a three-electrode system with Hg/HgO reference electrode putting in the fuel.

### 3. Results and discussion

#### 3.1. Optimization of single cell performance

In our previous study [6], it has been found that DBFC cell performance was significantly influenced by electrode performances, membrane thickness as well as cell structure. After optimization, we chose Nafion N112 membrane as the separator for preventing cathode from fuel crossover as it showed less ohmic resistance and suitable mechanical strength. Carbon-supported Pt electrodes were selected as the cathode as they showed good and stable performance. In this study, we report our new performance improvements by using composite anode materials. Fig. 3 illustrates the cell performance varying with the anode material. It is interesting to note that the combination of nickel powder, carbon-supported Pd and Nafion binder led to a double power density. It was also observed that combination of only two components did not yield the same result. It suggests that three materials led to a collaborative effect

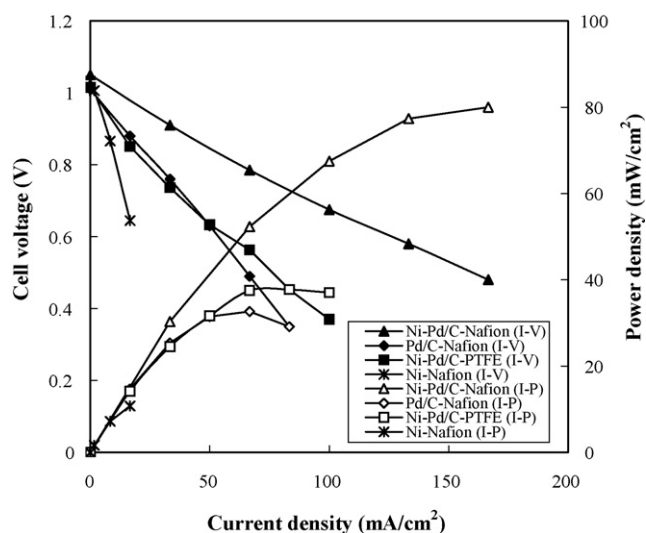


Fig. 3. Variation of cell power performance with the anode material. (Anode: composite catalysts  $20 \text{ mg cm}^{-2}$ , component ratios: (1) Ni: Pd/C:Nafion = 0.75:0.3:0.1, (2) Pd/C:Nafion = 0.6:0.1, (3) Ni: Pd/C:PTFE = 0.75:0.3:0.13, (4) Ni:Nafion = 1.5:0.1 membrane: N112, fuel: 5 wt.% NaBH<sub>4</sub> in 20 wt.% NaOH, working condition: passive mode at 298 K.)

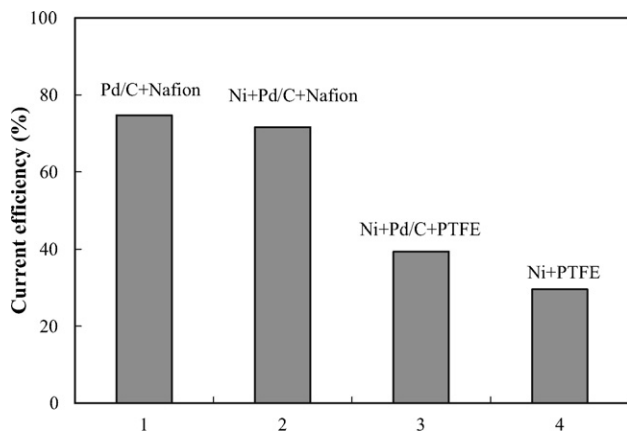


Fig. 4. Change of fuel current efficiency with the anode material. (Anode: composite catalysts  $20 \text{ mg cm}^{-2}$ , component ratios: (1) Pd/C:Nafion=0.6:0.1, (2) Ni:Pd/C:Nafion=0.75:0.3:0.1, (3) Ni:Pd/C:PTFE=0.75:0.3:0.13, (4) Ni:PTFE=2:0.1; membrane: N112; current density:  $50 \text{ mA cm}^{-2}$ ; fuel: 5 wt.%  $\text{NaBH}_4$  in 20 wt.%  $\text{NaOH}$ .)

on power performance. In our previous study, we found that borohydride oxidation on Ni and Pd showed different performances and mechanisms [13]. The nickel electrodes usually demonstrated more negative open circuit potential, small polarizations but a 4e reaction mechanism. The Pd electrodes showed less negative potentials but a higher current efficiency of 6e. We suppose that the electrochemical reaction taking place predominately on the Ni electrodes is the oxidation of hydrolysis product  $\text{BH}_3\text{OH}^-$  as this species shows the oxidation wave at the most negative potential among three possible oxidation species:  $\text{BH}_3\text{OH}^-$ , H and  $\text{BH}_4^-$  [15,28]. On the other side, the oxidation of atomic hydrogen may be the main electrochemical reaction on Pd surface. Therefore, the electrode with two kinds of electrocatalysts may take advantage of the both and thus showed a large improvement. It was also noted that Nafion addition played an important role in the enhancement. Nafion in the electrode formed a thin layer on the electrocatalyst surface. This thin layer may have two effects on electrode performance. First, Nafion as a hydrophilic material would improve the contact of fuel with the electrocatalysts and thus increase their utilization efficiency. Also the hydrophilicity of electrode might help to depress hydrogen evolution by increasing gas formation resistance. Another important role of Nafion is that it might reduce borohydride concentration on catalyst surface. Although the 6e reaction may take place on Pd surface, it only occurred at low borohydride concentrations [13]. Nafion film formed on electrode surface might form a concentration gradient. As a result, it is possible to achieve high current efficiencies at high  $\text{NaBH}_4$  concentrations. Fig. 4 shows fuel current efficiencies using different anode compositions. The fuel efficiency was calculated as follows:

$$\text{current efficiency} = \frac{\text{electricity obtained}}{(\text{initial NaBH}_4 \text{ amount} - \text{residual NaBH}_4 \text{ amount}) \times 5.67 \text{ Ah/g}} \times 100\%$$

It can be seen that high fuel efficiencies of more than 70% were achieved in Pd and Nafion containing electrodes. This result inspires us that it is possible to realize the desired performance

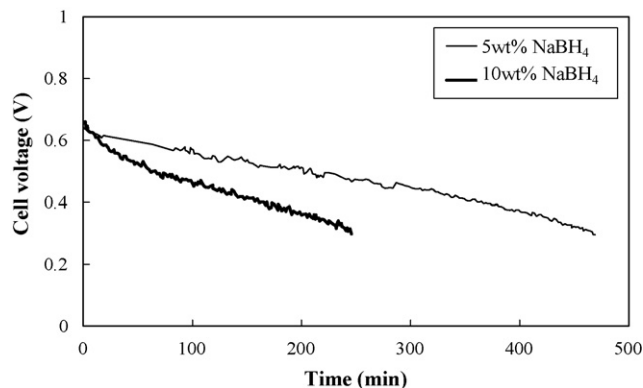


Fig. 5. Change of cell voltage with time for a 30 ml  $\text{NaBH}_4$  solution. (Anode: Ni-PTFE with Ni  $0.2 \text{ g cm}^{-2}$ , membrane: N115, current density:  $33 \text{ mA cm}^{-2}$ .)

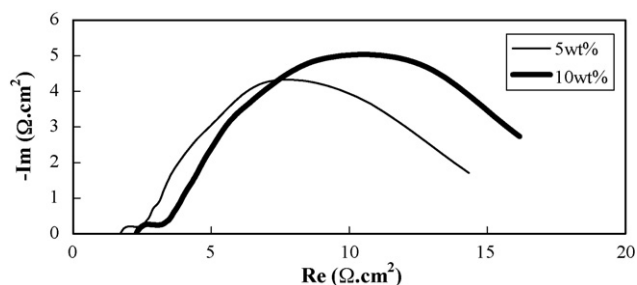


Fig. 6. Nyquist plots of the cathode under different borohydride concentrations. (Anode: Ni-PTFE with Ni  $0.2 \text{ g cm}^{-2}$ , membrane: N115.)

by combining more than one electrocatalyst and careful design of anode composition and structure.

Although high initial  $\text{NaBH}_4$  concentration is desirable in consideration of energy density of the DBFC system, it was found to be another factor significantly influencing cell performance. Fig. 5 shows cell voltage curves using 5 wt.% or 10 wt.%  $\text{NaBH}_4$  solution. It demonstrated that high  $\text{NaBH}_4$  concentration led to performance instability and decreased fuel efficiency. As the anode performance was improved in high  $\text{NaBH}_4$  concentrations [13], this phenomenon may be caused by some effects on membrane or cathode performance. Fig. 6 shows the impedance spectra for the cathode when using two  $\text{NaBH}_4$  concentrations. The intersection on the horizontal axis represents resistance from the electrolyte, here mainly from the membrane. The large semi-circle at low frequencies is attributed to the electrochemical reaction on the cathode. It can be seen from Fig. 6 that high borohydride concentration led to the increases in both electrolyte resistance and reaction impedance. Although the crossover rate of borohydride ions through Nafion membranes was shown at a level of  $4 \times 10^{-7} \text{ mol cm}^{-2} \text{ S}^{-1}$  (N117) [10], it demonstrated obvious effects on cathode performances [30]. As the increase of borohydride concentration will inevitably lead to increase in

fuel crossover, it is reasonable to attribute the performance instability to a higher rate of borohydride crossover to the cathode side.

### 3.2. Two-cell module

To make a practical power unit, it is necessary to connect a number of cells in series to obtain required voltage and power. The most common way for fuel cells is the stacking technology that uses bipolar plates to connect two cells electrically and at the same time supply fuel and oxidant for two adjacent cells. For liquid fuels, stacking of cells would inevitably need auxiliary facilities such as a pump for fuel delivery and a fan for air flowing, which would consume some power and make the system complicate and less compact [31]. Considering good performance exhibited by the DBFC single cell even at fully passive conditions, it is possible for us to make passive DBFC power modules to minimize system weight and volume. Therefore, we arranged cells in a planer way in which the cathodes facing outside can effectively breathe air. Also the anode side was made to contact with a fuel reservoir to realize a fully passive operation condition.

First a two-cell module shown in Fig. 1 was constructed and tested. As illustrated in Fig. 7, a maximum power density of  $75 \text{ mW cm}^{-2}$  was achieved, which is comparable to the single cell performance. In the planer arrangement, we found that it is possible for cells to share the electrolyte in one container without apparent loss. Also it was found that cells on one plane could share one membrane with no need to cut off from each other. It made the module structure very simple. Also it would be easy to fabricate and assemble this kind of module.

On the other side, it was found that two cells facing each other could not share one fuel container as a short-circuit would happen when two anodes were not distant enough. Therefore, it is necessary to separate the fuel container for cells on two facing planes.

### 3.3. Eight-cell module

After the two-cell module test, we prepared an eight-cell module. In this module, cell structure was further simplified

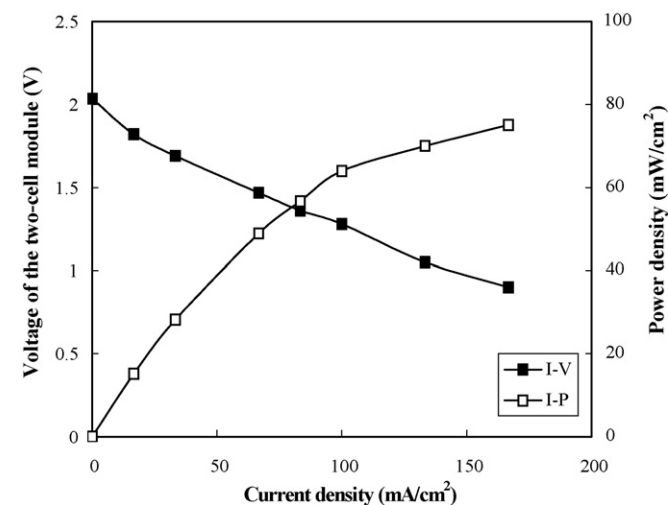


Fig. 7. Polarization curve and power performance for the two-cell module. (Anode: Ni–Pd/C–Nafion  $20 \text{ mg cm}^{-2}$ , membrane: N112, fuel: 5 wt.%  $\text{NaBH}_4$  in 20 wt.% NaOH.)

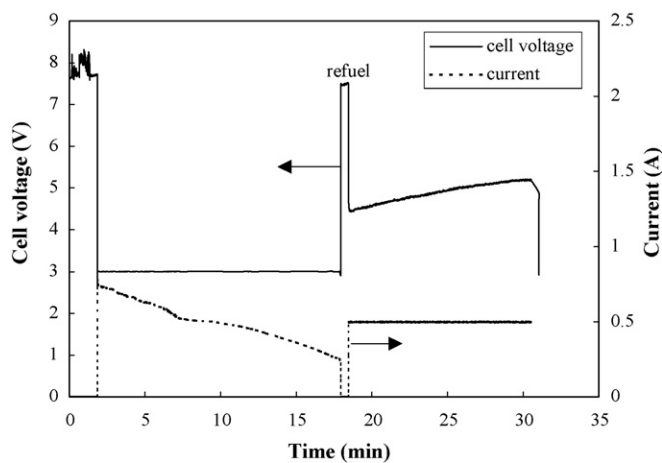


Fig. 8. Power generation from the eight-cell module under a constant voltage and a constant current mode. (Anode: Ni–Pd/C–Nafion  $20 \text{ mg cm}^{-2}$ , membrane: N112, fuel: 5 wt.%  $\text{NaBH}_4$  in 20 wt.% NaOH, working condition: passive mode at 298 k.)

as shown in Fig. 2. To reduce system weight, Au-plated nickel mesh replaced endplates to act as current collector and diffusion layer for fuel or air. Also in this module, four cells on one plane shared one piece of membrane and one fuel tank. But the tank was separated at the center for the two facing planes. Fig. 8 shows the performance of the module operated under a constant voltage mode and a constant current mode. With this structure, the module reached a stable power of 2.5 W. Fig. 9 illustrates that the module successfully powered a small TV set. However, the operation time was about 20 min due to the limited fuel volume and decreased fuel efficiency.

The very simple cell structure and good performance of the module make the DBFC very promising for practical applications. But there is still a large space for performance enhancement before commercialization. The most challenging problem would be further enhancement of power performance and current efficiency simultaneously, rather than tradeoffs between the two. Our results suggest that it may be realized by optimizing electrode composition and structure. Developments on membrane and cell structure are also indispensable.



Fig. 9. Photograph of the eight-cell module powering a small TV-set.

Increase of operational borohydride concentration would be another important issue as the energy density of the power system depends to a large extent on  $\text{NaBH}_4$  concentration in the fuel.

#### 4. Conclusions

The single cell performance of the direct borohydride fuel cell was further enhanced by anode modification. The power density reached  $80 \text{ mW cm}^{-2}$  under ambient and passive conditions. At the same time, fuel efficiency was also improved because of the addition of carbon-supported Pd and Nafion ionomer. High borohydride concentration was found to induce instability of performance due to fuel crossover. Therefore, the cell exhibited better performance under 5 wt.% than 10 wt.%  $\text{NaBH}_4$ . On the basis of single cell improvements, power modules of two cells and 8 cells in a planer design were prepared with simplified structures. Good performance of modules suggests that DBFC is very promising for portable applications.

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