



Influences of hydrogen evolution on the cell and stack performances of the direct borohydride fuel cell

B.H. Liu^a, Z.P. Li^{a,*}, J.K. Zhu^a, S. Suda^b

^a College of Materials Science and Chemical Engineering, Zhejiang University Hangzhou 310027, PR China

^b Materials & Energy Research Institute Tokyo, Ltd., 1-1 Sawarabi-daira Tateshinachuo-kogen, Kitayama, Chino-shi, Nagano, Japan

ARTICLE INFO

Article history:

Received 17 March 2008

Received in revised form 27 April 2008

Accepted 28 April 2008

Available online 7 May 2008

Keywords:

Direct borohydride fuel cell

Single cell

Stack

Performance

Hydrogen evolution

ABSTRACT

To scale up power generation of the direct borohydride fuel cell (DBFC), 10-cell and 20-cell stacks have been constructed based on the single cell achievements. It has been found that the stacking loss of the DBFC is mainly caused by hydrogen evolution which leads to uneven fuel distribution in each cell of the stack. To reduce stacking loss, several efforts have been made to decrease hydrogen evolution influence on the stack performance. The anode preparation method has been modified from a dry-method to a wet-method. The influence of hydrogen evolution on stack performance can be alleviated by altering fuel supply manner. When hydrogen evolution is suppressed, an even distribution of cell voltage can be obtained and the maximum power of 10-cell stack reaches up to 229 W.

© 2008 Elsevier B.V. All rights reserved.

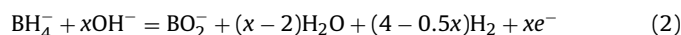
1. Introduction

Borohydrides are considered as potential fuels for fuel cells due to their high energy densities [1–5]. Recently many investigations focus on reaction mechanism, catalyst development and single cell performance of the direct borohydride fuel cell (DBFC) [6–17]. However, there are few detailed reports related to the DBFC stack technology.

It is considered that the stack performance is determined not only by the single cell performance but also by mass transport during operation. It is known that gaseous hydrogen would be produced from borohydride hydrolysis reaction during operation [17]:



as well as anodic reaction of borohydride:



Blockage of certain channels caused by hydrogen bubbles in anode side is considered to be a critical problem for the performance improvement of the DBFC stack because hydrogen bubbles would block channels in flow field and thus decrease the effective reaction area.

Ha and co-workers tried to improve stack performance by decrease of hydrogen evolution influence through suitable anode shape design [18] and flow field improvement [19]. We have successfully assembled the panel DBFC stacks using 2 cells or 8 cells to generate 1 W or 4 W of electricity [20]. In this paper, we assembled a series of DBFC stacks based on our single cell achievements. The effects of anode catalyst, anode structure and membrane thickness on the cell performance and hydrogen evolution during operation were investigated. The influences of hydrogen evolution on stacking loss were investigated and discussed by modifying anodes and fuel supply manner.

2. Experimental details

An alkaline sodium borohydride solution (containing 10 wt.% of NaBH₄, 5 wt.% of NaOH) was used as a fuel for the DBFC. We developed two kinds of anode preparation method: dry-method and wet-method. In the dry-method, anodes were prepared by mixing sugar (pore formation agent) with Ni powders (Inco. 210), surface-treated Zr–Ni alloy (FMH) and PTFE (binder), then pasting the mixture onto the Ni foam. The weight ratio of sugar:Ni powder:FMH:PTFE was 0.5:0.25:0.25:0.3. Electrodes were roll-pressed into a plate with a size of L84.6 × W80 and 0.5 mm in thickness and then sugar was washed away by water to leave micropores in the catalyst layer as shown in Fig. 1. These micropores built a hydrogen passage network in three-dimension. The anode contained 150 mg cm⁻² of catalyst (Ni and Zr–Ni alloy). The preparation

* Corresponding author. Tel.: +86 571 87951977; fax: +86 571 87953149.
E-mail address: zhoupengli@zju.edu.cn (Z.P. Li).

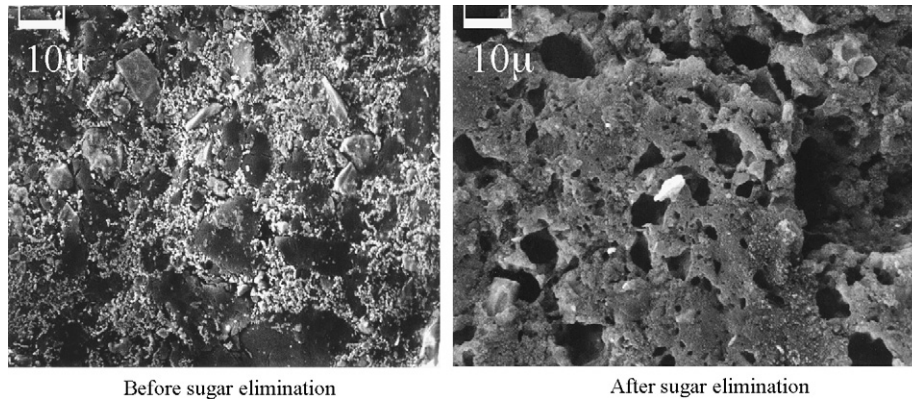


Fig. 1. Anode structures before and after sugar elimination.

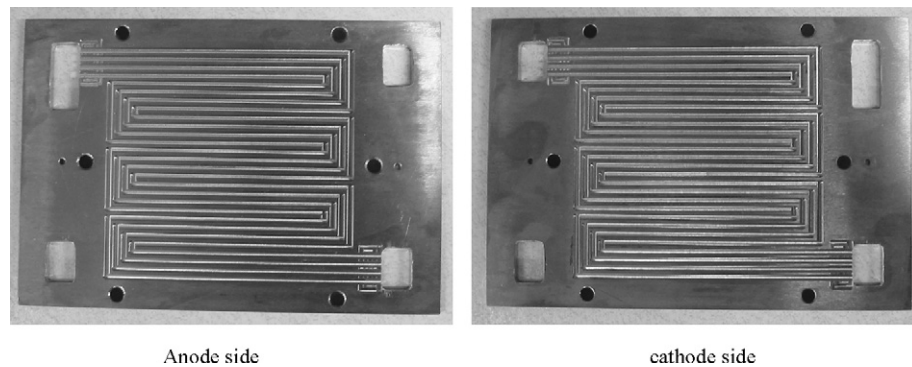


Fig. 2. Four-channel serpentine flow fields at anode and cathode side.

of the surface treated Zr–Ni alloy was the same as that of negative electrode materials in Ni–MH batteries [21].

In the wet-method, anode ink was prepared by mixing Ni powders, FMH and carbon supported Pd (Pd/C contains 10 wt.% of Pd) with 5 wt.% Nafion solution (weight ratio of Ni powder:FMH:Pd/C:Nafion = 0.75:0.75:0.6:0.3). The ink was pasted into a piece of Ni-foam with thickness of 0.9 mm to increase the porosity of the anode. In order to suppress the hydrogen evolution during operation, the catalyst loading was decreased to 15 mg cm^{-2} of catalyst (Ni, FMH and Pd).

The cathode catalyst was 50 wt.% Pt supported on Vulcan XC-72. The catalyst was pasted on a PTFE-treated TOREY™ graphite fiber paper with 1 mg cm^{-2} Pt loading. Nafion membranes were used for separating anode from cathode. Nafion membranes were pretreated by boiling in 3 wt.% of H_2O_2 solution for 1 h and then boiling in de-ionized water for 1 h.

316 Stainless steel was used for making bipolar plates. Serpentine flow field was applied to expel hydrogen bubbles in anode side and liquid in cathode side. Four-channel serpentine flow field was applied for both anode side and cathode side as shown in Fig. 2. Fig. 3 shows the stack measurement set-up.

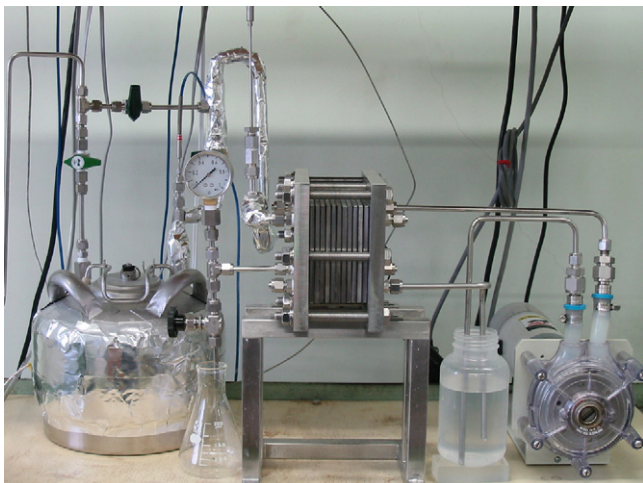


Fig. 3. DBFC stack measurement set-up.

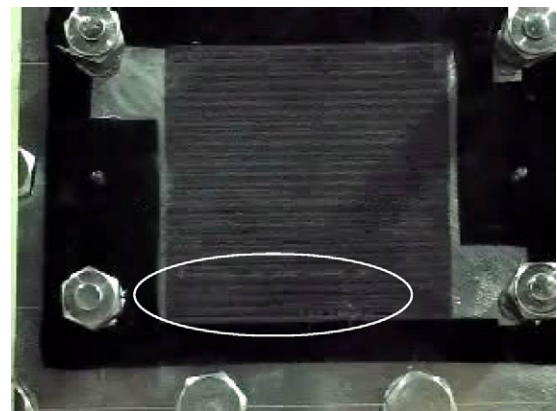


Fig. 4. Observation of hydrogen bubbles blocked in channels through anolyte flow simulation.

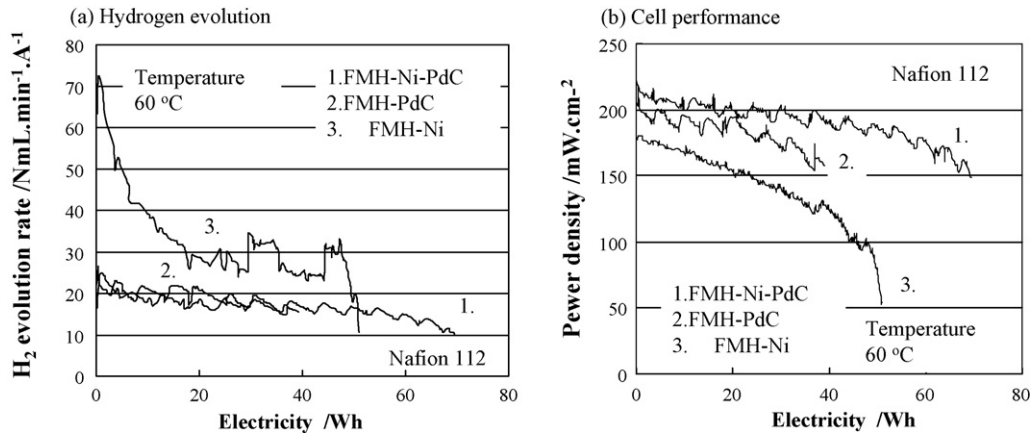


Fig. 5. Effects of Pd addition on the power density and hydrogen evolution during operation at current of 30 A. NaBH₄: 100 g; fuel flux: 0.15 L min⁻¹; air flow rate: 5 L min⁻¹.

3. Results and discussion

Stack performance is determined by single cell performance and mass transportation in each cell of a stack. In order to obtain a good stack performance, it is necessary to improve single cell performance by designing of a better cell configuration.

3.1. Single cell performance

It is known that the voltage drop of a fuel cell is caused by activation losses, fuel crossover and internal currents, ohmic losses and concentration losses. Here we investigated the effects of anode catalyst, anode structure and Nafion membrane thickness on reducing the ohmic losses to improve the cell performance of the DBFC.

3.1.1. Anode

Comparing with our previous results in the small test cell [7], it was found that the maximum power density was decreased from 190 mW cm⁻² to 50 mW cm⁻² when the anode area was enlarged from 6 cm² to 68 cm². Through anolyte flow observation in a transparent cell, we saw that hydrogen bubbles blocked channels and thus hinder the anolyte flow as shown in Fig. 4. It implied that hydrogen bubbles would also accumulate between anode and membrane to hinder the ion immigration from anode to cathode. As a result, the effective reaction area was decreased.

In order to prevent accumulation of hydrogen bubbles in the anode channels, we tried to prepare anodes by the wet-method

and decreasing the catalyst loading to suppress hydrogen evolution. A power density of 180 mW cm⁻² was achieved when using FMH-Ni as the catalyst of the anode with area of 68 cm² though the hydrogen evolution rate still kept at a high level as shown in Fig. 5.

When we added Pd/C into the anode, it was found that hydrogen evolution was effectively suppressed as shown in Fig. 5(a) and the cell performance was improved as shown in Fig. 5(b). This result confirmed the effects of Pd/C addition in the anode of the DBFC on depression of hydrogen evolution and improvement of cell performance [17].

3.1.2. Membrane thickness

Fig. 6 shows single cell performances of the DBFC when using Nafion membranes with different thickness. It was found that the open circuit voltages (OCV) of the DBFC were decreased

Table 1

Effects of Nafion membrane thickness on the OCV and resistance of the DBFC during operation when using FMH-Ni anode

Nafion membrane	Thickness (mm)	OCV (V)	R (Ω cm ²)
117	183	1.215	5.44
115	127	1.180	4.81
1135	89	1.140	2.65
112	51	1.118	1.91
211	25.4	1.108	1.26

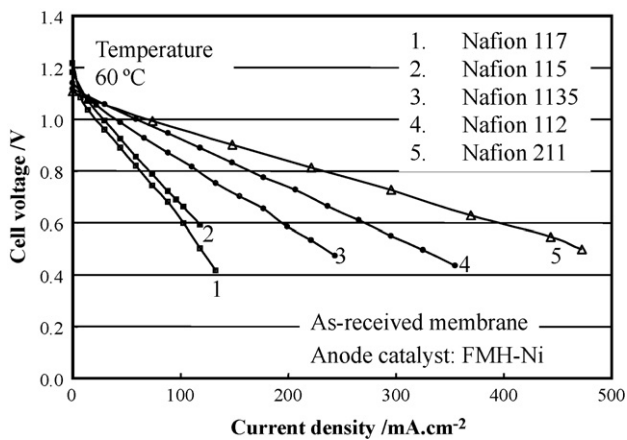


Fig. 6. Cell operation voltages when decreasing of the applied membrane thickness. Fuel flux: 0.15 L min⁻¹; air flow rate: 5 L min⁻¹.

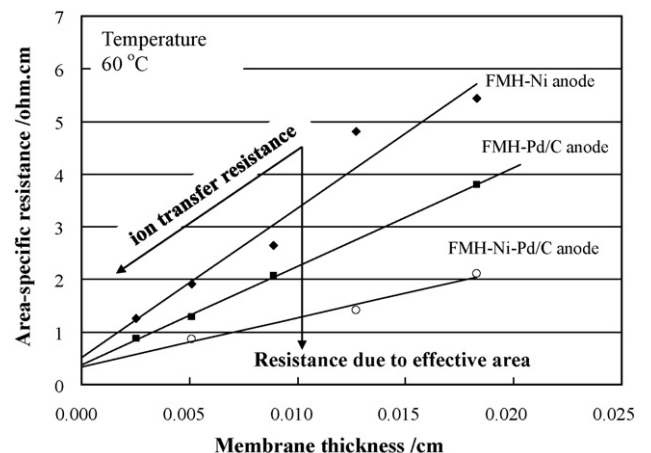


Fig. 7. Increase of the cell resistance vs. the membrane thickness.

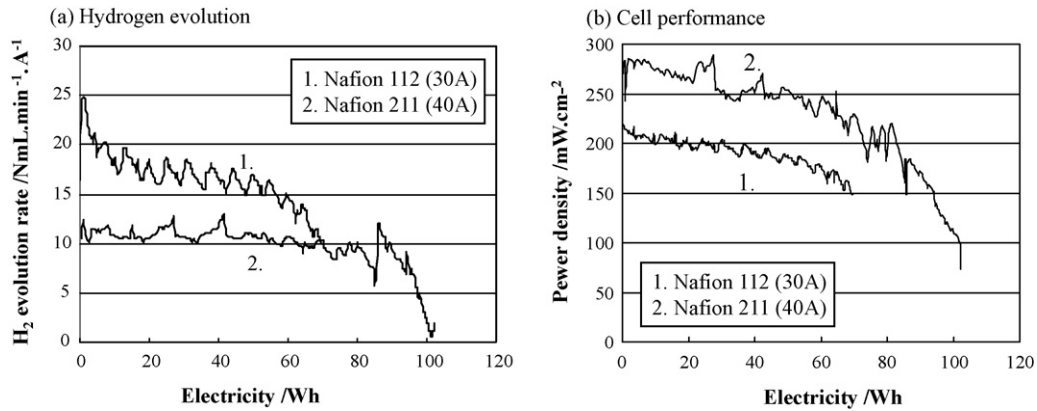


Fig. 8. Power density and hydrogen evolution rate during operation. H₂O₂-treated membrane; anode catalyst: FMH-Ni-PdC. Temperature: 60 °C; NaBH₄: 100 g; fuel flux: 0.15 L min⁻¹; air flow rate: 5 L min⁻¹.

with decreasing of the applied membrane thickness, but cell performances were improved when using thinner membranes as the electrolyte. It was considered that the decrease of OCV was caused by BH₄⁻ crossover. The thinner the used membrane, the more serious the crossover would become. The cell performance improvement can be attributed to the decrease of cell ohmic resistance when using thinner membranes as described in next

paragraph. From Fig. 6, it can be known that the cell voltage of the DBFC demonstrated a linear relation to the operation currents so that the total ohmic resistance of the DBFC can be calculated from data fitting. The calculation results are tabulated in Table 1.

From Table 1, it was found that the resistance decreased with decreasing of the membrane thickness, which can be attributed to the decrease of ion transfer resistance (along the line) during operation as shown in Fig. 7. It was also found that the cell resistance demonstrated small slopes (vertical direction) when using FMH-PdC and FMH-Ni-PdC anodes as shown in Fig. 7, implying that adding Pd in anode decreased the ohmic resistance due to effective area because Pd would consume gaseous hydrogen according to our previous result that Pd in the anode can electro-oxidize the generated hydrogen [17]. The DBFC can be operated at a larger current when using thinner membrane so that Pd can consume more gaseous hydrogen. As a result, the ohmic resistance due

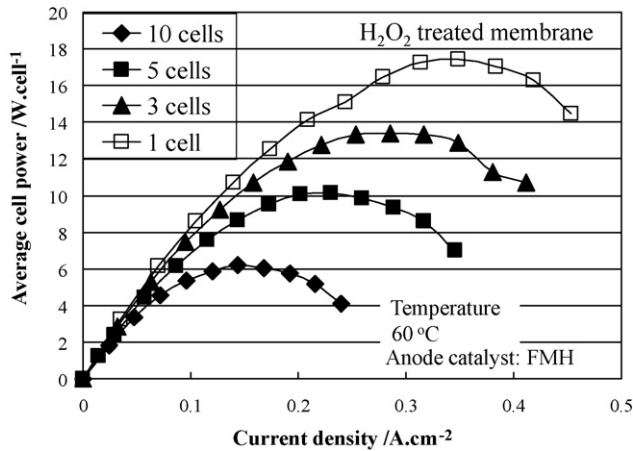


Fig. 9. Stacking loss of when increasing cells in the DBFC stack. Fuel flux: 0.15 × NL min⁻¹; air flow rate: 5 × NL min⁻¹, N, cell number in the stack.

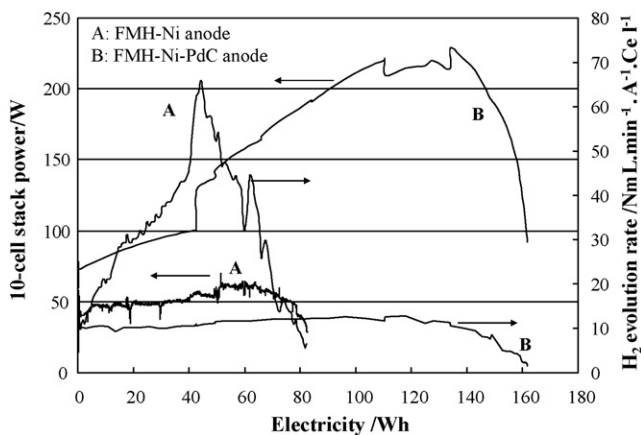


Fig. 10. Relation of power vs. hydrogen evolution rate of the 10-cell stack. Membrane: H₂O₂-treated Nafion 211. Starting temperature: 20 °C. Fuel flux: 1 L min⁻¹; air flow rate: 40 L min⁻¹. NaBH₄: 100 g.

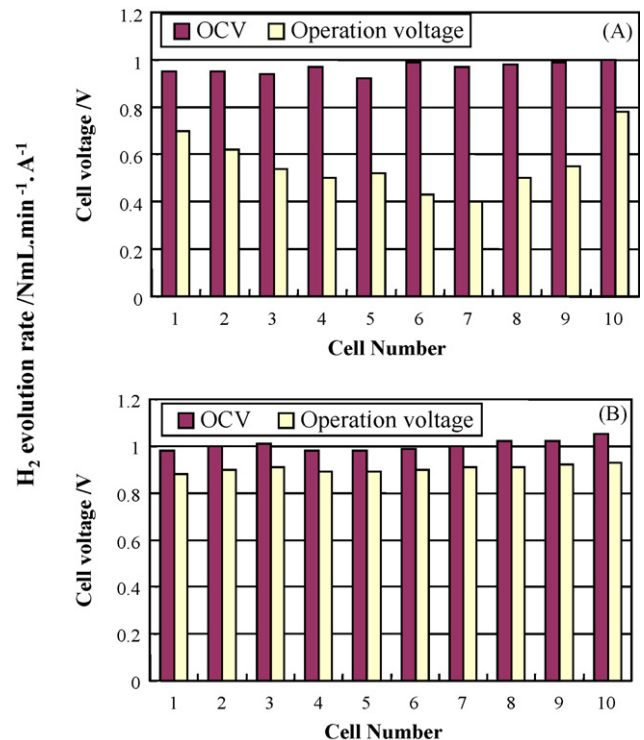


Fig. 11. Voltage distributions of the 10-cell stack during operation at 10A. (A) FMH-Ni anode; (B) FMH-Ni-PdC anode.

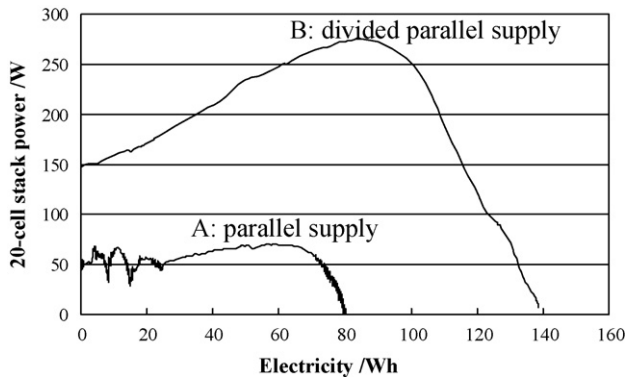


Fig. 12. Performance improvement of the 20-cell stack by changing fuel supply in the stack. Starting temperature: 20 °C, fuel flux: 1.5 L min⁻¹; air flow rate: 50 L min⁻¹. NaBH₄: 100 g.

to effective area was decreased. That is why the cell with higher hydrogen evolution rate demonstrated a lower power density as shown in Fig. 5(b).

Fig. 8 shows hydrogen evolution and cell performance during operation when using FMH–Ni–Pd/C as the anode catalyst and Nafion 112 and 211 membranes as the electrolyte. It was found that hydrogen evolution was depressed and cell performance was improved when the operation current was increased to 40 A by using 211 membrane. Due to the large operation current when thinner membrane (N211) was used, Pd would consume more gaseous hydrogen. As a result, the hydrogen evolution was depressed, and NaBH₄ utilization was improved.

3.2. Stack performance

We assembled the DBFC stacks with 3, 5 and 10 cells using FMH–Ni anodes prepared by the dry-method. It was found that

the average cell power densities of the DBFC stacks were decreased with increasing the cell number as shown in Fig. 9. A big stacking loss occurred. The hydrogen evolution rate during operation of the 10-cell stack and the relevant stack power are shown in Fig. 10. It can be seen that the hydrogen evolution rate was increased compared to single cell as shown in Fig. 5(a). We measured the operation voltage distributions of the 10-cell stack when operation at current of 10 A as shown in Fig. 11. It was found that the stack demonstrated an uneven distribution in operation voltage. Middle cells in the stack showed lower operation voltages. It was considered that this uneven distribution in operation voltage was mainly brought by the hydrogen bubble blockages in the middle cells of the stack due to the hydrogen evolution from the anodes.

Then we assembled the stack using FMH–Ni–PdC anodes prepared by the wet-method. It was found that the stack demonstrated an even distribution in cell voltage and stack power reached up to 229 W as shown in Fig. 10. Meanwhile hydrogen evolution rate was decreased significantly.

We tried to further increase the cells in the stack. A 20-cell stack was assembled. However, a big stacking loss occurred again as shown in Fig. 12. Then we tried to change fuel flow in the stack to decrease the stacking loss. The 20-cell stack was divided into two blocks. Each block has 10 cells. We changed the fuel flow direction from the 11th cell of the stack as shown in Fig. 13. It was found that stacking loss was significantly decreased and the stack power reached up to 274 W. It implied that the hydrogen evolution influence on the stack performance could be reduced by changing the fuel supply in the stack. However, we have not known the reason yet. Further investigations are needed. Because the stack power is still lower than the double power of the 10-cell stack, it indicates that hydrogen evolution still influences the stack performance. Therefore, more efforts on the development of anode catalyst are necessary to improve the stack power of the DBFC by depressing hydrogen evolution.

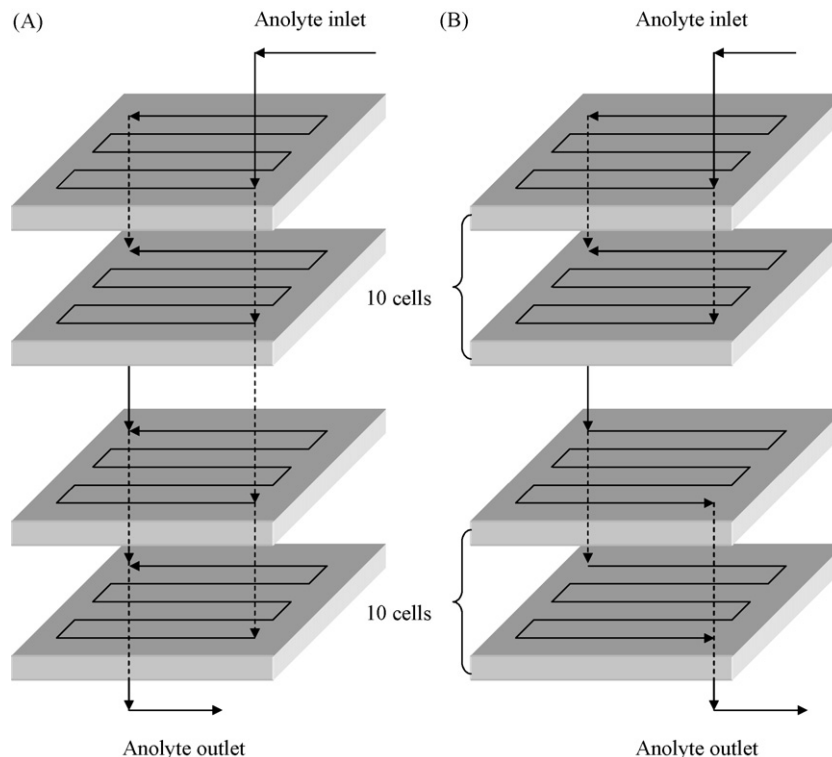


Fig. 13. Fuel supplies in the 20-cell stack. (A) Parallel supply; (B) divided parallel supply.

4. Conclusions and remarks

Two kinds of anode preparation method (dry-method and wet-method) were developed. Adding Pd/C catalyst in anode can decrease the hydrogen evolution rate and improve the stack power of the DBFC. Increase of operation current by using thinner Nafion membranes can effectively suppress hydrogen evolution during operation.

The hydrogen evolution was one of the most critical problems to the performance improvement of the DBFC stack. The stacking loss of the DBFC was mainly caused by hydrogen evolution, which resulted in an uneven fuel distribution between the cells of the stack. When hydrogen evolution was suppressed, the stack showed an even distribution in operation voltage and stack performance was significantly improved. The hydrogen evolution influence on the stack performance can be reduced by changing the fuel supply in the stack.

As hydrogen evolution would decrease not only the DBFC performance but also 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 but no hydrolysis reaction occurs. On the other hand, more efforts should be made in optimization of flow field design and improvements of anode structure such as forming hydrophobic pore.

Acknowledgements

This work is financially supported by Hi-tech Research and Development Program of China (863), grant Nos. 2006AA05Z120

and 2007AA05Z144. Doctoral fund from Education ministry of China (20070335003) and Fund from Science & Technology ministry of Zhejiang province (2007R10029).

References

- [1] R.L. Pecsok, *J. Am. Chem. Soc.* 76 (1953) 2862–2864.
- [2] W.H. Stockmayer, D.W. Rice, C.C. Stephenson, *J. Am. Chem. Soc.* 77 (1955) 1980–1983.
- [3] R. Jasinski, *Electrochem. Tech.* 3 (1965) 40.
- [4] M.E. Indig, R.N. Snyder, *J. Electrochem. Soc.* 109 (1962) 1104–1106.
- [5] M.V. Mirkin, H. Yang, A.J. Bard, *J. Electrochem. Soc.* 139 (8) (1992) 2212–2217.
- [6] S. Amendola, P. Onnerud, M. Kelly, P. Petillo, S. Sharp-Goldman, M. Binder, *J. Power Sources* 84 (1) (1999) 130–133.
- [7] Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Electrochem. Soc.* 150 (2003) A868–A872.
- [8] B.H. Liu, Z.P. Li, S. Suda, *J. Electrochem. Soc.* 150 (2003) A398–A402.
- [9] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, *J. Power Sources* 126 (1–2) (2004) 28–33.
- [10] J.-H. Kim, H.-S. Kim, Y.-M. Kang, M.-S. Song, S. Rajendran, S.-C. Han, D.-H. Jung, J.-Y. Lee, *J. Electrochem. Soc.* 151 (7) (2004) A1039–A1043.
- [11] B.H. Liu, Z.P. Li, S. Suda, *Electrochim. Acta* 49 (2004) 3097–3105.
- [12] E. Gyenge, *Electrochim. Acta* 49 (2004) 965–978.
- [13] B.H. Liu, Z.P. Li, S. Suda, *Electrochim. Acta* 50 (2005) 3719–3725.
- [14] H. Dong, R. Feng, X. Ai, Y. Cao, H. Yang, C. Cha, *J. Phys. Chem. B* 109 (21) (2005) 10896–10901.
- [15] B.H. Liu, S. Suda, *J. Alloys Compd.* 454 (2008) 280–285.
- [16] Z.P. Li, B.H. Liu, K. Arai, S. Suda, *J. Alloys Compd.* 404–406 (2005) 648–652.
- [17] Z.P. Li, B.H. Liu, J.K. Zhu, S. Suda, *J. Power Sources* 163 (1) (2006) 555–559.
- [18] C. Kim, K.-J. Kim, M.Y. Ha, *J. Power Sources* 180 (1) (2008) 154–161.
- [19] C. Kim, K.-J. Kim, M.Y. Ha, *J. Power Sources* 180 (1) (2008) 114–121.
- [20] B.H. Liu, Z.P. Li, S. Suda, *J. Power Sources* 175 (1) (2008) 226–231.
- [21] Z.P. Li, E. Higuchi, B.H. Liu, S. Suda, *J. Alloys Compd.* 293–295 (1999) 593–600.