Short communication

A study on performance stability of the passive direct borohydride fuel cell

Bin Hong Liu [a,*], Zhou Peng Li [a], S. Suda [b]

[a] College of Materials and Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Materials & Energy Research Institute Tokyo Ltd., 1-1 Sawarabi-Daira, Tateshina-Chuokogen, Kitayama, Chino-shi, Nagano 391-0301, Japan

ABSTRACT

The performance stability of the direct borohydride fuel cell (DBFC) working under passive conditions was studied in this work. The stability within hours was found to be greatly affected by mass transport properties of different cell components. It was significantly improved by modifying electrode structures, increasing hydrophobicity of the cathode and using pretreated membranes. On the other hand, the stability of the DBFC cell for more than 100 h was determined by the durabilities of these cell components. The nickel anode and silver cathode were found to degrade after prolonged operations and thus the durabilities of these non-noble metal catalysts need to be improved.

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1. Introduction

Worldwide concern on energy security and environment pollution has stimulated the rapid development of fuel cell technologies. However, commercialization of hydrogen fuel cells has to overcome several obstacles including high cost and hydrogen storage. As an efficient and cost-effective system has not yet been established to produce, store and transport hydrogen, it is hoped that developments of direct liquid fuel cells could circumvent the hydrogen storage problem. In view of fuel energy density, cell performance and fuel safety, the direct borohydride fuel cell (DBFC) is a very promising liquid fuel cell [1–21]. It generates power according to the following reaction:

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e^- \qquad (1)$$
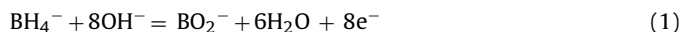
The DBFC offers higher cell voltage than hydrogen fuel cells. Development of the DBFC is currently focused on improving power density and fuel efficiency [10–21]. By optimizing electrode compositions and structures for both the anode and cathode, the power density of the DBFC has been increased to 250 mW cm^{-2} at temperatures around 60 °C [15], or higher than 100 mW cm^{-2} at room temperature in passive cells [20]. Fuel efficiency could also be improved by using Au or Au alloys [1,3,13], employing bi-metallic

anode catalysts [15,20], or adding some agents like thiourea to depress hydrogen evolution [3,17,20].

Besides power density, performance stability is another important property in DBFC development. A good initial performance does not guarantee a stable and repeatable performance over a long operation. But in practical applications, it is essential to achieve reliable and repeatable cell performance. The direct borohydride fuel cell differs from hydrogen fuel cells in many aspects due to their different chemistries. Many factors were found to influence performance stability of the DBFC. In this study, we report our efforts in improving performance stability of the passive DBFC by adjusting electrode or cell structure, and modifying cell materials. The results would help understanding electrochemical and mass transport processes in the DBFC configuration and inspire further DBFC developments.

2. Experimental details

The anodes of the DBFCs were prepared by first mixing and grinding nickel powder (INCO Inc., type 210) with polytetrafluoroethylene (PTFE) powder at a weight ratio of 1:0.05 in a mortar, and then filling the formed paste into a piece of nickel foam. The Ni catalyst loading was 0.2 g cm^{-2}. The cathodes were prepared by spreading carbon supported Pt or Ag catalysts (Pt 30 wt% or Ag 20 wt% on Vulcan XC-72 from E-Tek Corp.) on Toray carbon paper TGP-H-060. The catalyst loading of the cathodes was Pt 1 mg cm^{-2} or Ag 1.6 mg cm^{-2}. Cathodes were also made by using

* Corresponding author. Tel.: +86 571 87951770; fax: +86 571 87951770.
E-mail address: liubh@zju.edu.cn (B.H. Liu).

other substrates such as nickel felt and nickel foam (2 mm thickness). The substrates were first pretreated by immersing in diluted PTFE solution (10%) and then heating to 350 °C for 1 h under argon atmosphere to obtain water-proof property. Then the ink containing carbon supported Pt catalyst and PTFE was painted on the pretreated substrate materials. After drying at room temperature, the cathodes were further heated under argon atmosphere to 350 °C for 1 h.

Nafion N117, N115 and N112 membranes were used to separate fuel from the cathode but allow ion transfer from the anode to the cathode. The membrane was pretreated by boiling in 3% H_2O_2 solution and de-ionized water each for 1 h successively.

The structure of single cell was described in our previous paper [4]. The cell 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 the anode side 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 cm^2.

The fuel was prepared by dissolving sodium borohydride (Finnish Chemicals, 98% purity) in 20 wt% sodium hydroxide solution. Unless specially indicated, the fuel contained 5 wt% NaBH$_4$. The cells were operated in a fully passive condition without any pumps and other auxiliary facilities. The tests in all the research were carried out at room temperature around 25 °C and ambient conditions.

The performance stability of the DBFC was evaluated by monitoring cell voltages at constant currents when the fuel tank was initially filled with a 30 ml batch of borohydride solution. When NaBH$_4$ in the tank was near exhaustion, the test was interrupted for refueling and then restarted.

The cyclic voltammetry analysis was performed on Zahner IM6 electrochemical workstation. A Hg/HgO reference electrode encapsulated by N117 Nafion film was put in the anolyte tank during the measurements. The electrodes were scanned at a rate of 10 mV s^{-1} between −1 V and 1 V vs. Hg/HgO.

3. Results and discussion

It is desirable for the DBFC to demonstrate stable output during prolonged power generation. For the cell with definite fuel volume (30 ml in this work), it is hoped that the cell voltage could keep stable until NaBH$_4$ in the fuel is near exhaustion. Also the performance could be repeatable after the refueling. In this research, we divided the performance stability of DBFC into short-term and long-term stability. While short-term stability refers to performance stability within hours during operation, long-term stability denotes the stability for longer than 100 h. Short-term and long-term stability of the DBFC were found to be governed by different factors.

3.1. Short-term stability

3.1.1. Effects of the anode side

The anode structure was found to greatly influence the short-term stability of the DBFC. Fig. 1 shows that the densely packed Ni anode induced a very quick decrease in cell voltage when it was tightly pressed onto the membrane. To find the reason, the anode was deliberately taken apart from the membrane by about 5 mm. The cell voltage became stable after the adjustment. It suggests that alkaline sodium borohydride solution diffused into the anode not as easily as hydrogen gas due to high viscosity of the liquid fuel. If pores in the anode were not large enough, the anode catalyst could not sufficiently contact with the solution. Also hydrogen evolution on the anode increased diffusion resistance for borohydride solution.
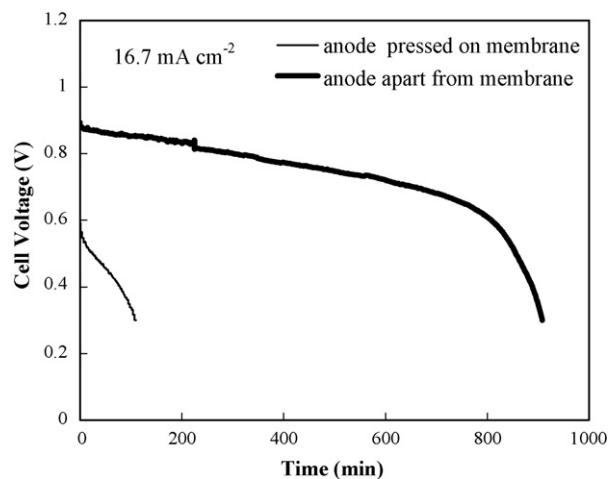

Fig. 1. Time dependences of cell voltage in different cell structures (N117 membrane, cathode: Pt 1 mg cm^{-2}).

Hydrogen bubbles also induced electrolyte deficiency between the anode and membrane. As a result, cell voltage became unstable due to insufficient ion transport and increased ohmic resistance at the anode side. Therefore, the anode in the DBFC should be more porous and with larger pores than that in hydrogen fuel cells to ensure full contact of the catalyst with the liquid fuel.

The borohydride concentration in the fuel was found to be another factor influencing performance stability. As can be seen from Fig. 2, the cell demonstrates faster decrease when using a 10 wt% NaBH$_4$ solution than a 5 wt% NaBH$_4$ solution. For the test with 10 wt% NaBH$_4$ fuel solution, the remaining solution still contained 5 wt% NaBH$_4$ after the cutoff voltage of 0.3 V. Increasing current density did not change this behavior. As reported in our previous paper [18], these results may be attributed to effects of NaBH$_4$ concentration on the membrane and/or cathode. With increasing NaBH$_4$ concentration in the fuel, its crossover to the cathode side would become severer and thus deteriorate cathode performance. Although Pt/C cathodes showed some tolerance of borohydride crossover [18], 10 wt% NaBH$_4$ concentration might induce a crossover level with which the Pt/C cathode could not manage.
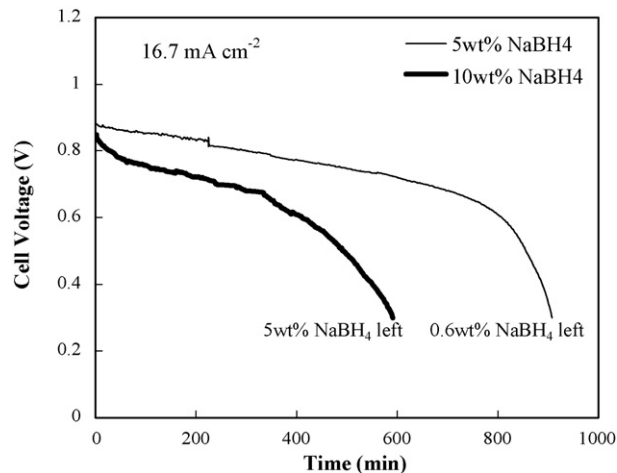

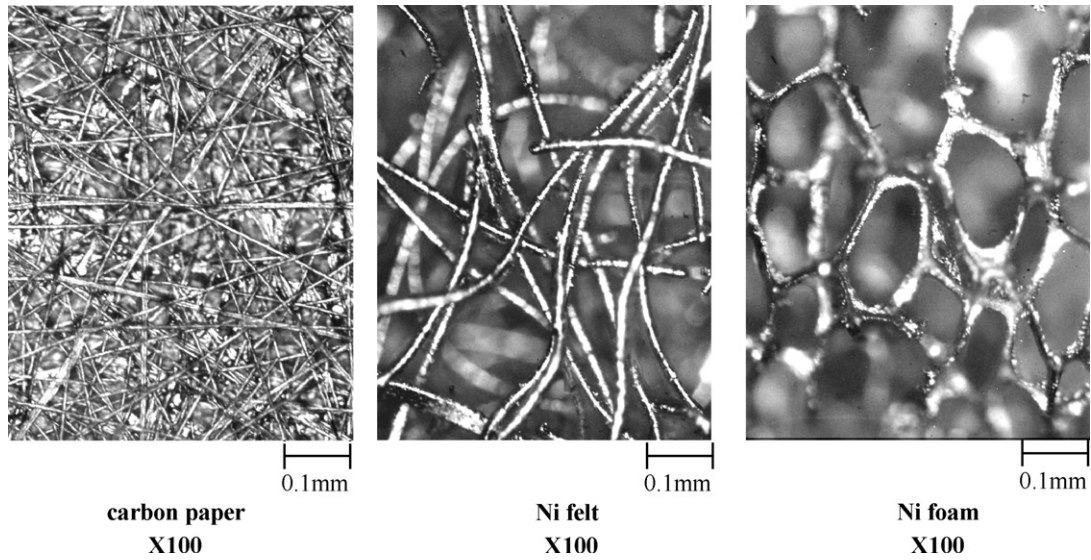**Fig. 2.** Effect of borohydride concentration on DBFC cell voltage (N117 membrane, cathode: Pt 1 mg cm^{-2}).

Fig. 3. SEM photos of three cathode substrates.

3.1.2. Effects of the cathode side

The mass transport property of the cathode also affected performance stability of the DBFC. As NaOH was produced on the cathode of the DBFC using the Nafion membrane [4], the cathode should have the ability to get rid of NaOH product to avoid electrode flooding. It is especially important for the passive cell as the product could not be carried away by the forced air flow. In this research, NaOH was rejected to the gas side of the cathode through the hydrophobicity of the electrode. To effectively discharge the NaOH product, three conductive materials were tested as the substrates of the cathode: carbon paper, nickel foam and nickel felt. Fig. 3 shows the SEM observations on three materials. It demonstrates that the nickel foam and felt had larger pores than the carbon paper. The cell test also revealed that the larger porosity led to more stable cell voltage as shown in Fig. 4. It suggests that large pores in the diffusion layer of the cathode would facilitate the discharge of the NaOH product.

It was found that the hydrophobicity of not only the cathode but also the cell plate on cathode side would influence the performance stability. Our results showed that the endplate on the cathode side should also possess water-proof property otherwise the cathode would suffer from the flooding problem.

3.1.3. Effects of the membrane

The property of Nafion membrane was also found to influence the performance stability of the DBFC. Fig. 5 shows time dependence of cell voltage with a N115 membrane. The H_2O_2/H_2O pretreated membrane revealed higher and more stable voltage than the untreated one. It suggests that the pretreatment ensured a stable ion transport property of the membrane.

3.1.4. Effects of current density

Current density applied in the DBFC cell is another important factor influencing cell performance stability. The cell voltage under a high current density may be unstable even though it is stable under low current densities, as mass transport loss increases at high current densities. After the modifications of the cell components described above, stable performance was achieved at different current densities as shown in Fig. 6. The cell voltage under these currents kept almost stable, with slow drops caused by the gradual decrease of $NaBH_4$ concentration in the tank. The final rapid drop was due to the near exhaustion of $NaBH_4$ in the fuel. The fuel efficiencies were calculated to be in a range of 18–27% in these tests according to the obtained electricity shown in Fig. 6, the consumed $NaBH_4$ amount and a theoretical value of 5.6 Ah for 1 g of $NaBH_4$ from Eq. (1). As studied in our previous paper [10], the theoreti-
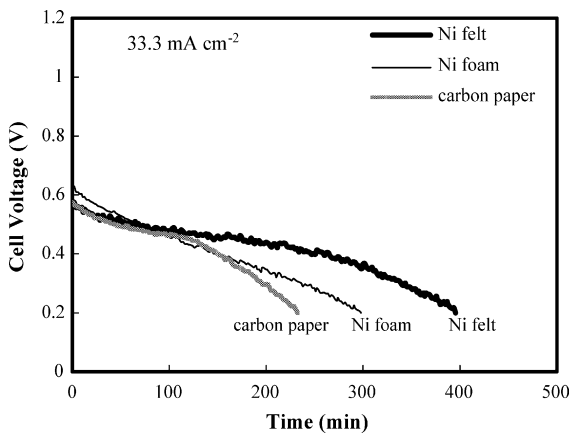

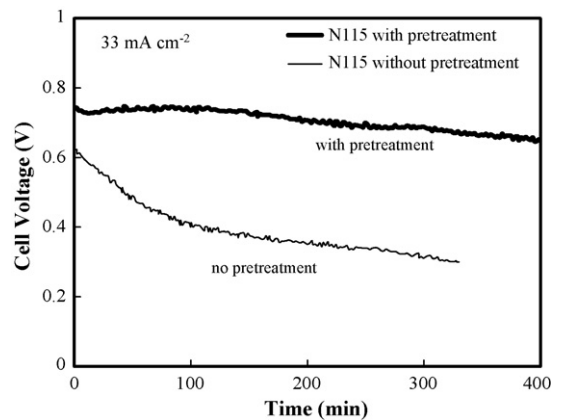**Fig. 4.** Effect of the cathode substrate material on cell voltage stability (N117 membrane, cathode: Pt 1 mg cm^{-2}).

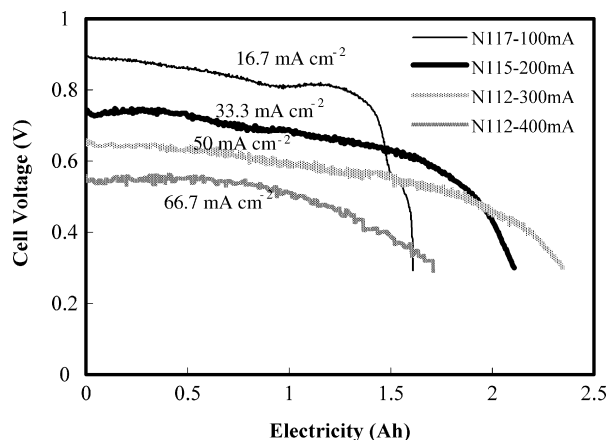**Fig. 5.** Effect of membrane pretreatment on cell voltage stability (N115 membrane, cathode: Pt 1 mg cm^{-2}).

Fig. 6. Cell performance stability under different current densities (cathode: Pt 1 mg cm^{-2}).

Fig. 7. Change of polarization for the porous Ni electrode (used Ni electrode: after working at excessive polarization conditions for more than 10 h).

cal fuel efficiency for the Ni anode is 50%, which is achievable at high current densities. The low fuel efficiency obtained in the test was thus mainly due to the low current density attainable in the cell.

Above results demonstrate that the short-term performance stability of DBFC was mainly determined by mass transport properties of different cell components. The anode should be porous enough for full contact of catalyst with the fuel. Also the anode structure should ensure a quick release of the evolved hydrogen gas in case its accumulation in the electrode decreases the effective area and ion transfer to the membrane. The cathode side should have a proper hydrophobic/hydrophilic balance as water is a reactant at the cathode but flooding should be avoided. The membrane should give stable ion transport property.

3.2. Long-term stability

While the short-term stability of DBFC performance was mainly governed by mass transport properties of different cell components, the long-term performance stability was found to be dependent on the durabilities of these components.

One of big advantages of the DBFC is that non-noble materials can be used as its anode and cathode catalysts. For example, Ni or Ni-based alloys are found to exhibit good performance by offering small polarizations and high current densities. However, the porous Ni electrode made by fine Ni-powder was found to gradually increase its polarizations as shown in Fig. 7. The reason may be that stable oxide or hydroxide was formed during operation. It has been found that Ni electrodes suffered from passivation at potentials above −0.6 V vs. Hg/HgO. The main reason is its surface oxidation under this potential. NaBH$_4$ is a strong reducing agent, but it was found inadequate to reduce the nickel hydroxide under these conditions. Therefore, the gradually increased polarization during fuel cell operation was presumably caused by the formation of surface oxide.

In our previous study, Ag cathodes were applied in the DBFC [4,18]. Although the Ag/C cathode exhibited comparable power performance as the Pt/C cathode, it was found to be less tolerant to fuel crossover than the Pt/C cathode and suffered from degradation especially after operation interruptions. It has been reported that the Ag cathode demonstrated considerable stability with only 100 mV potential decrease after 5000 h continuous operation in alkaline H$_2$/O$_2$ fuel cells [22]. The reasons for the slight aging were the decrease of surface roughness and decomposition of PTFE binder. On the other hand it was also reported that Ag shows a
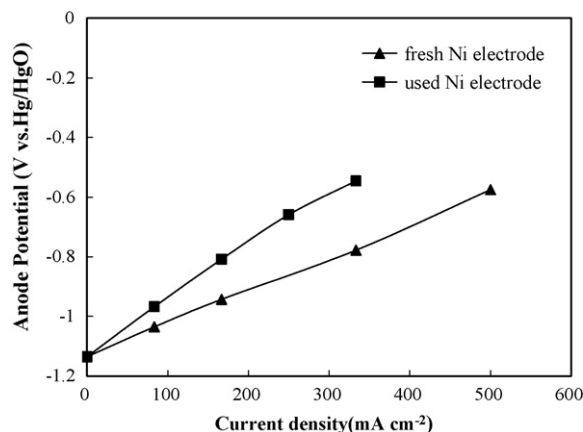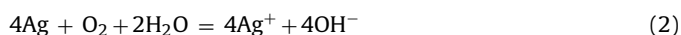
strong dissolution at the open circuit condition [23]:

$$4Ag + O_2 + 2H_2O = 4Ag^+ + 4OH^- \tag{2}$$

Ag$^+$ dissolved in the electrolyte would be precipitated on the anode and thus influence cell performance.

As the Ag cathode was reported to show only slight aging in alkaline H$_2$/O$_2$ fuel cells, the reason for its degradation in DBFC needs to be further investigated. Fig. 8 shows the cyclic voltammetry analysis results of the Ag cathode in the DBFC cell before and after the degradation. The degraded electrode not only showed a decreased current density of the oxygen reduction reaction, but also revealed new peaks between 0 V and 0.5 V vs. Hg/HgO, which were not observed in the CV curve of the fresh prepared electrode. The peaks were presumably related with the following reaction:

$$2Ag + 2OH^- = Ag_2O + H_2O + 2e \tag{3}$$
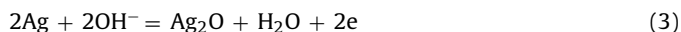
The presence of the new peaks suggests that the cathode surface became easy to suffer from oxidation under open circuit condition. This alteration of the cathode might induce its performance degradation.

The Pt cathode showed some tolerance to fuel crossover and demonstrated considerable stability in our previous research [18]. But its longer durability needs to be further investigated as its hydrophobicity might deteriorate during prolonged operations.
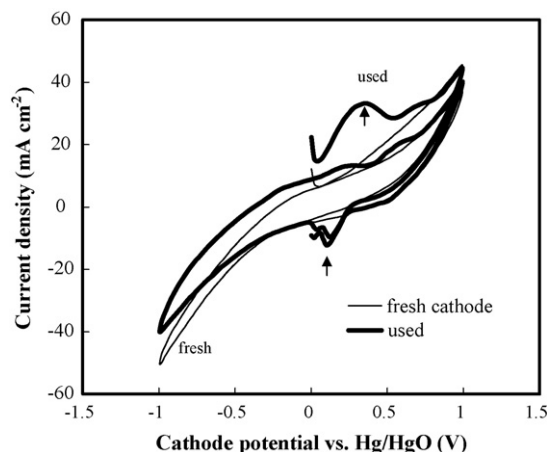

Fig. 8. Cyclic voltametry analysis of the Ag cathode in the DBFC cell before and after degradation (cathode: Ag 1.6 mg cm^{-2}).

The membrane stability may also influence the performance stability of DBFCs. Although Nafion membrane is supposed to be stable in alkaline medium, its durability in DBFCs needs to be investigated.

4. Conclusions

In order to develop the direct borohydride fuel cell into a viable technology, the effects influencing its performance stability were studied in this research. The stability of the DBFC cell within hours was found to be greatly affected by the mass transport properties of different cell components. The porosities of the anode and cathode supporting materials, the membrane pretreatment and borohydride concentration had significant influences on performance stability. By modifying the structures and materials of the cell, the short-term performance was significantly stabilized. On the other hand, the long-term stability of the cell for hundreds of hours depended on the durabilities of these cell components. The nickel anode gradually increased its polarization presumably due to the formation of nickel hydroxide on the surface. The silver cathode suffered from surface oxidation at operation rests. Therefore the durabilities of these non-noble metal catalysts need to be improved.

Acknowledgement

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