Short communication

Depression of hydrogen evolution during operation of a direct borohydride fuel cell

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Abstract

Hydrogen evolution from the anode usually occurs during operation of a Direct Borohydride Fuel Cell (DBFC). This would not only decrease the fuel utilization, but also lower the cell performance because hydrogen bubbles would hinder ion movement in the anolyte. In this paper, the hydrogen evolution behavior is investigated based on relations of hydrogen evolution rates versus operation currents of the DBFC. The effects of anode modification on the hydrogen evolution rate and the cell performance were investigated. It was found that hydrogen evolution was depressed by adding Pd, Ag and Au catalysts in the anode. Coating a thin Nafion film on the catalyst surfaces was another effective way to decrease the hydrogen evolution rate. Depression of the hydrogen evolution and improvement of the DBFC performance can be achieved by adding carbon supported Pd in Ni anode with a suitable content of Nafion. However, too much Nafion in the anode would degrade the DBFC performance.
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1. Introduction

Borohydride has been considered a potential fuel for fuel cells due to its high energy density [1–7]. For example, the theoretical energy density of sodium borohydride reaches up to 9.3 Wh g^{-1}-NaBH$_4$, which is higher than that of methanol (6.1 Wh g^{-1}-MeOH). Some fundamental research on the Direct Borohydride Fuel Cell (DBFC) has been reported [4,5,8–19]. Recent progress on the DBFC has been summarized in review articles [20,21].

However, hydrogen evolution usually occurred during operation of the DBFC. It not only decreased the fuel utilization, but also lowered the cell performance because hydrogen bubbles would hinder ion movement in the anolyte. There are several published papers describing hydrogen evolution during operation of the DBFC [8,13,14,17,22,23]. Here we summarize the hydrogen evolution behavior based on the relation of hydrogen

evolution rate to the operation current of the DBFC in order to find a way to depress hydrogen evolution.

Cell performance is an important issue for the DBFC. It is desirable to depress hydrogen evolution without impairing cell performance. In this paper, we investigate the effects of anode modification on hydrogen evolution rate and cell performance by using a mixture of Ni and carbon supported precious metal catalysts. A new method by which a thin Nafion film formed on the anode catalyst surfaces, is suggested to depress hydrogen evolution when the DBFC is operated at high temperature with a highly concentrated borohydride solution as the fuel.

2. Hydrogen evolution during operation of the DBFC

In a DBFC configuration, gaseous hydrogen may be produced from the borohydride hydrolysis reaction:

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \tag{1}$$
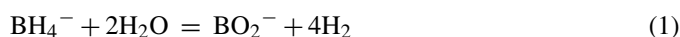
and anodic reaction of the borohydride:

$$BH_4^- + xOH^- = BO_2^- + (x-2)H_2O + (4 - 1/2x)H_2 + xe^- \tag{2}$$
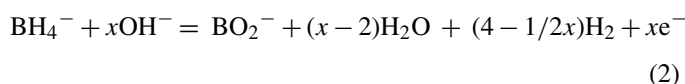
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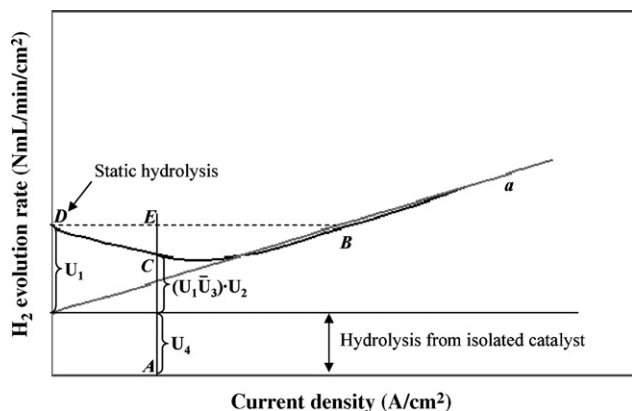*E-mail address:* zhoupengli@zju.edu.cn (Z.P. Li).

Fig. 1. Schematic hydrogen evolution behavior during operation of the DBFC. $(U_1\bar{U}_3)U_2$ is a logic function, which means $(U_1$ NOT $U_3)$ OR U_2.

It was found that the coulombic number x in reaction (2) strongly depended on the anode materials [17]. A typical relation of the hydrogen evolution rate to the current density is illustrated in Fig. 1. Point **D** is the hydrogen evolution rate at the open circuit condition where only borohydride hydrolysis takes place (static hydrogen evolution rate). Linear line **a** stands for the hydrogen evolution from the borohydride electrooxidation. Curve **DCB** represents a typical relation of hydrogen evolution rate versus current density. From our previous results, the rate of hydrogen evolution from the Ni anode was almost a constant (line **DEB**) before the line reached the electrooxidation line (line **a** at point **B**) (ref. [17], Fig. 4 (a)). However, Pd and Pt showed different behavior which has a minimum in the hydrogen evolution rate (ref. [17], Fig. 5(a) and 6(a)). It can be deduced that, when using Pd or Pt as the anode catalyst, there was a hydrogen consumption process:

$$4H_2 + 8OH^- = 6H_2O + 8e^- \tag{3}$$

Therefore, there would be three possible reactions occurring on catalyst sites during operation of the DBFC. They are borohydride hydrolysis reaction (1) whose H_2 evolution rate is U_1, the borohydride electrooxidation reaction (2) whose H_2 evolution rate is U_2 and the hydrogen electrooxidation reaction (3) whose H_2 consumption rate is U_3. They compete with each other.

It was considered that usually there are some catalyst particles isolated from the electrode without contact with other electrical conductors. Neither borohydride electrooxidation nor hydrogen electrooxidation occurrs on these particles, but borohydride hydrolysis reaction takes place. Therefore, the hydrogen evolution rate during operation of the DBFC could be written as:

$$R = (U_1\bar{U}_3)U_2 + U_4 \tag{4}$$

U_4 stands for the hydrogen evolution rate due to borohydride hydrolysis from the isolated catalysts. Eq. (4) is a logic function which means $(U_1$ NOT $U_3)$ OR U_2 AND U_4. According to Eq. (4), a quasi-8e-reaction could occur $(U_1\bar{U}_3 = U_2 = 0)$ if we designed an anode where reaction (1) and reaction (3) occurred. An intrinsic 8e-reaction means $U_1 = U_2 = U_3 = 0$. Therefore, it can be deduced that hydrogen evolution would be effectively depressed by decrease of the isolated catalysts and use of catalysts on which BH_4^- ions could be electro-oxidized by an intrinsic 8e-reaction or quasi-8e-reaction.

On the other hand, we found that the borohydride concentration is another important factor in determination of the reaction mechanism according to our previous results. A quasi-8e-reaction occurred at Pt anode when using $NaBH_4$ alkaline solution (<1 M) as the anolyte [17]. We supposed that in the case of high concentration of $NaBH_4$ (on the catalyst surface, the amount of BH_4^- ions is much greater than the amount of catalytic sites for BH_4^- electrooxidation), when a tetrahedral BH_4^- ion absorbs on a Pt surface, only one H^- in tetrahedral BH_4^- ion contacts the Pt. The other three H^- would be surrounded by H_2O. When the absorbed H^- was electro-oxided, the other three H^- would react with H_2O to generate hydrogen gas. As a result, a 2e-reaction reaction occurred. With decreasing $NaBH_4$ concentration, two H^- in the tetrahedral BH_4^- ion would be absorbed on the Pt. As a result, a 4e-reaction would occur. However, for a tetrahedral BH_4^- ion absorbed on the Pt surface, only three H^- maximum could be absorbed on the catalytic sites at same time. Therefore, a 6e-reaction would be the limit for BH_4^- electrooxidation. In the case of a low concentration of $NaBH_4$ (on the catalyst surface, amount of BH_4^- ions less than the amount of catalytic sites for BH_4^- electrooxidation), there would be extra catalysts. These extra catalytic sites could be used for H_2 electrooxidation. As a result, a quasi-8e-reaction would occur.

According to the anodic behavior of the borohydride ion [22], a low ratio of BH_4^- concentration to OH^- concentration is favorable to reaction (2) with a high x value because highly concentrated NaOH solution can stabilize BH_4^- ions [27]. Nafion as a cation exchange polymer is a poor anion conductor, and can function as a barrier for BH_4^- movement because the Nafion membrane can effectively separate the BH_4^- ions from anode to the cathode in our cell [12]. We expected that Nafion additions to the anode could decrease the isolated catalysts and lower the borohydride concentration at the catalyst sites.

3. Experimental details

A borohydride solution containing 10 wt.% $NaBH_4$ was prepared by dissolving sodium borohydride (purity: 98%) in 20 wt.% of NaOH solution (NaOH purity: 98%). Ni powder (Inco. 210) and carbon supported precious metal (Pd, Au, Ag: 10 wt%) on Vulcan XC-72 were used as the anode catalyst. The anode was prepared by mixing Ni powders with carbon supported precious metals, dispersing in 2.5 wt.% PTFE or 2.5 wt.% Nafion solution, and then pasted into Ni foam with thickness of 0.9 mm before drying. The loading of the anode catalyst was 15 mg cm^{-2}.

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 112 membrane was used for separating anolyte from cathode. Nafion membrane was treated by immersing the membrane in boiling 3 wt% of H_2O_2 for 1 h then washing with deionized water before Na^+ exchange.
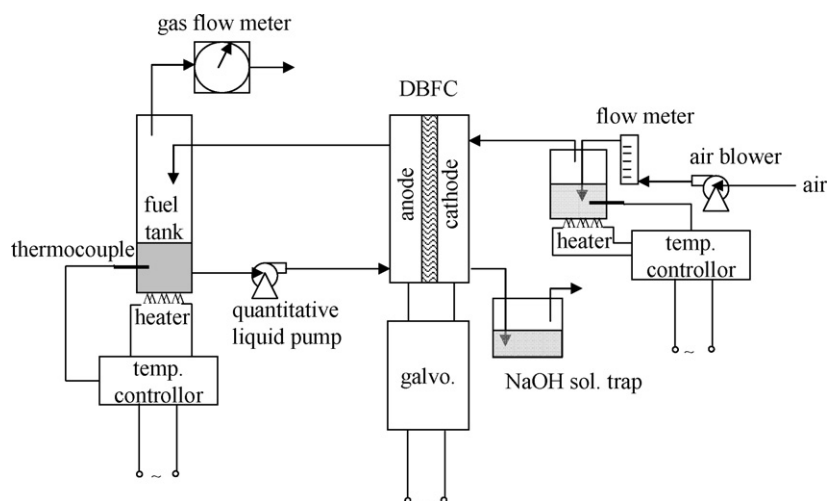
Fig. 2. Test system scheme.

4. Experimental results and discussion

4.1. Nafion addition

A 4-channel serpentine flow pattern was applied to the cell end plates (both anode and cathode sides) with an effective area of $100 \, cm^2$ ($8 \, cm \times 12.5 \, cm$). Cell performance were measured at $0.15 \, L \, min^{-1}$ of fuel flow rate, $5 \, L \, min^{-1}$ of air flow rate at operation temperature $60 \,°C$. Air humidification was conducted by bubbling method at the same temperature. The test system was illustrated in Fig. 2.

Nafion addition to the PEMFC or DMFC electrodes is usually employed to improve ion conductivity. Kim et al. have reported that the Nafion addition in the anode of a DBFC (content less than 25 wt%) improved the cell performance at room temperature due to reduction of the interfacial resistance [19], however they did not mention the effect on the depression of the hydrogen evolution from anode. From our previous results, it is found that borohydride concentration would change the electrooxidation mechanism of borohydride [17]. A low concentration of borohydride would be favorable to reaction (2) with a high x value. Here, we tried to lower the borohydride concentration on catalysts by forming a Nafion film on catalysts through adding Nafion in the anode. Fig. 3 shows the Nafion addition effects on hydrogen evolution at $60 \,°C$ compared with PTFE addition. It was found that Nafion addition in anode could depress hydrogen evolution not only from the hydrolysis reaction but also from the electrochemical reaction. It was noted that there was an intercept through extrapolation of hydrogen evolution rate versus current density at large currents as shown in Fig. 3. The hydrogen evolution from borohydride hydrolysis due to isolated catalysts, decreased with increasing the Nafion content in anode. When the Nafion addition content reached up to 20 wt%, an apparent 6e electrooxidation behavior was observed.

According to our previous results, when using borohydride solution as the fuel at low concentration ($<1 \, M$ of $NaBH_4$), the hydrogen evolution rate of the Pd anode was located at average value between 6e- and 8e-reaction (ref. [17], Fig. 4), whereas the borohydride electrooxidation mechanism on Ni surfaces did not change with change of borohydride concentration (ref. [17], Fig. 5). Fig. 5 showed a schematic borohydride con-
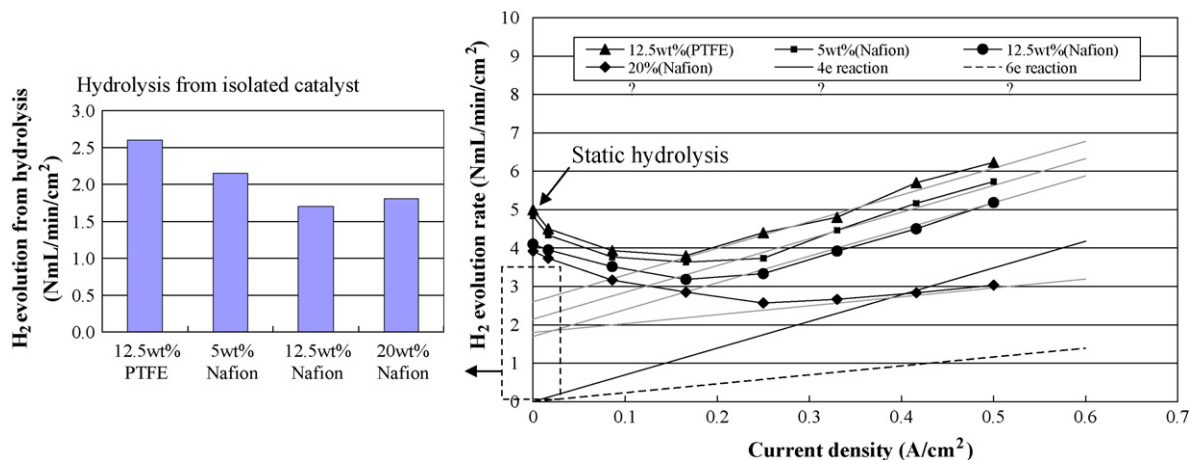

Fig. 3. Effect of Nafion addition on H_2 evolution. Anode: $14.4 \, mg \, Ni + 0.6 \, mg \, Pt \, cm^{-2}$; cathode: $1 \, mg \, Pt \, cm^{-2}$, fuel rate: $0.15 \, mL \, min^{-1}$; air flow rate: $5 \, L \, min^{-1}$, temperature: $60 \,°C$.
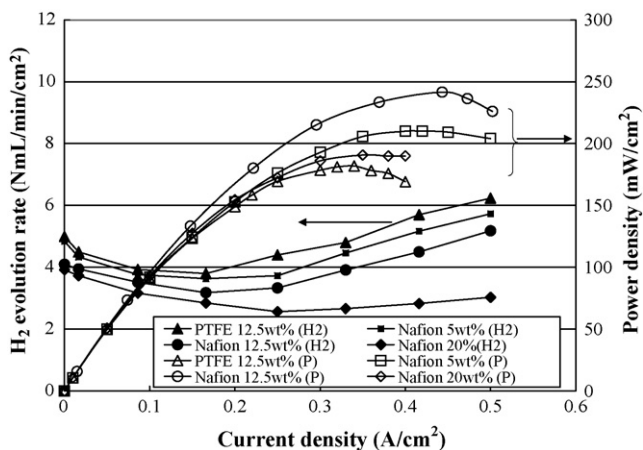
Fig. 4. Effect of Nafion addition effects on H_2 evolution and cell performance. Anode: 14.4 mg Ni + 0.6 mg Pd/cm^2, cathode: 1 mg Pt/cm^2, fuel rate: 0.15 mL/min, air flow rate: 5 L/min, temperature: 60 °C.

Fig. 6. Secondary catalyst addition effects on H_2 evolution depression and cell performance. Anode: 14.4 mg Ni + 0.6 mg precious metal cm^{-2}, Nafion content: 12.5 wt%, fuel rate: 0.15 mL min^{-1}, air flow rate: 5 L min^{-1}, temperature: 60 °C.

centration distribution at Nafion-coated Pd surface. Borohydride concentration would decrease with increasing coated Nafion film thickness according to the Fick's law of diffusion. Therefore, this apparent 6e reaction occurred at Ni-Pd anode, might be caused by a predominated 6e-reaction took place on Pd catalyst particles.

We linked the hydrogen evolution rate with the cell power density as shown in Fig. 4. It was found that Nafion addition not only depressed the hydrogen evolution but also improved the cell performance when Nafion content was less than 12.5 wt% (including catalyst, carbon black and binder). However, the power density decreased when adding too much Nafion in the anode (in our case: 20 wt%). We supposed that higher Nafion content in anode resulted in a large mass transfer resistance, though it favored for depression of hydrogen evolution. Therefore, we have to adjust Nafion content in the anode of the DBFC
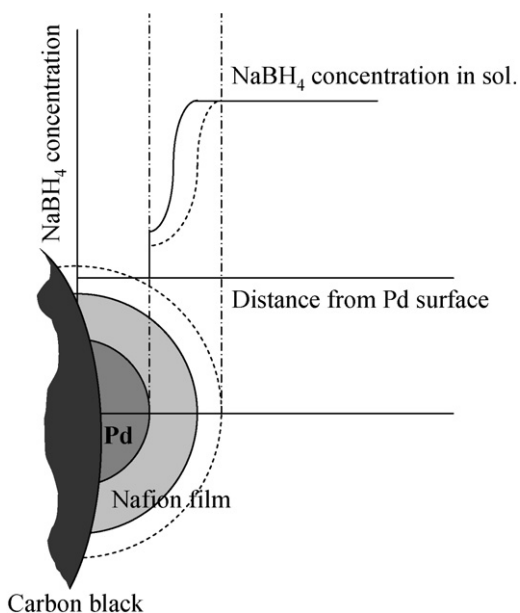

Fig. 5. Schematic borohydride concentration distribution on a Nafion-coated Pd surface.
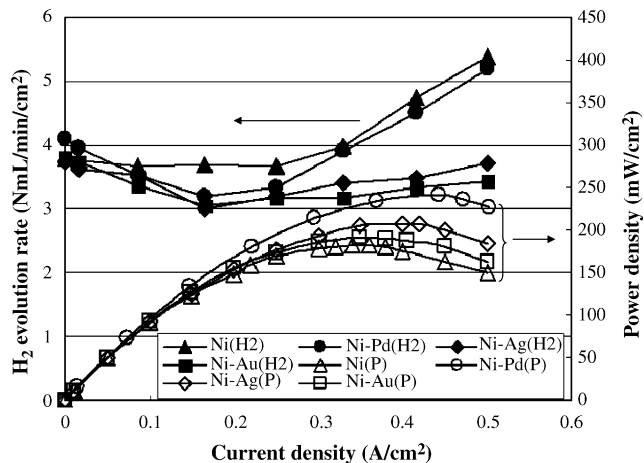
to balance depression of hydrogen evolution, decrease of isolated catalysts with increase of mass transfer resistance.

4.2. Anode catalyst

Amendola mentioned that Au electrode demonstrated a high columbic efficiency [5] and Atwan et al. used colloid Au and Au-alloy [24] to improve cell performance; however, the power density was usually below 100 mW cm^{-2}. Our previous results showed that Pd electrode can decrease the hydrogen evolution at a certain condition [17], but has not linked the hydrogen evolution rate with power density. Here, we tried to modify anode composition by using Ni and carbon supported precious catalyst mixture to study the relation of hydrogen evolution with power density of the DBFC. Fig. 6 shows the secondary catalyst addition effects on the hydrogen evolution rate and cell performance. It was found that hydrogen evolution rate on Ni-Pd, Ni-Ag and Ni-Au anode decreased with increasing the current density, comparing with static borohydride hydrolysis. Hydrogen evolution rate of Ni-anode kept unchanged before it hit to the 4e electrooxidation line. This agreed with our previous results obtained at room temperature [17]. Ag and Au showed a higher depression against hydrogen evolution than Pd anode. It can be attributed to that borohydride would electro-oxidized in 8e-reaction on Au according to the Amendola's result [5]. The Ag-added anode demonstrated a similar hydrogen evolution behavior of Au. It is hard to determine the borohydride electrooxidation mechanism on the Ag surface. A more detailed investigation is needed. Comparing with Pd addition, the Ag and Au additions to the anode degraded cell performance.

Because borohydride electrooxidation and borohydride hydrolysis are very similar in mechanism [22,23], it is difficult to find a suitable catalyst that has a high electrochemical activity but poor catalytic activity for borohydride hydrolysis. Good catalysts for the electrochemical reaction of borohydride usually are good catalysts for borohydride hydrolysis. Therefore, a reasonable solution to the hydrogen evolution problem is to find catalysts where hydrogen gas can be electro-oxidized
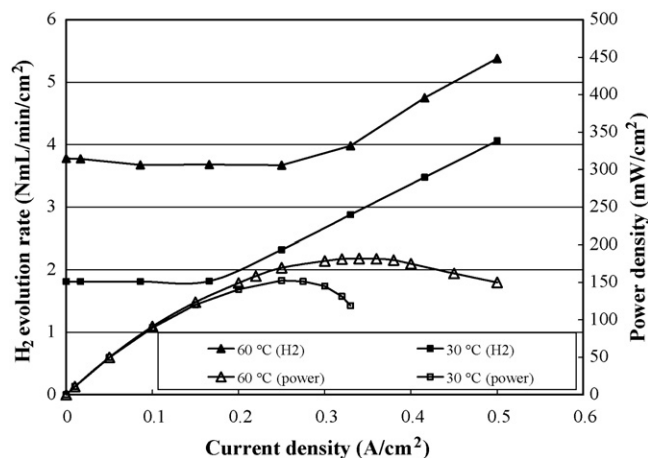
Fig. 7. Influence of operation temperature on H_2 evolution and cell performance. Anode: 15 mg Ni cm^{-2}, fuel rate: 0.15 mL min^{-1}, air flow rate: 5 L min^{-1}.

according to reaction (3). It is known that Pt and Pd are the best catalysts for hydrogen electro-oxidation. Gyenge et al. reported that Pt-Ir and Pt-Ni were the most active anode catalysts [25]. Detailed research work on Pt or Pd is needed to explore the possibility of a quasi-8e-reaction through modification of the anode composition.

4.3. Operation temperature

Schlesinger et al. have reported that the rate of borohydride hydrolysis decreases with decreasing hydrolysis temperature [26]. It was thought that hydrogen evolution would be depressed by a decrease of operation temperature of the DBFC. Fig. 7 shows the influence of operation temperature on the hydrogen evolution rate on the Ni anode and cell performance. It was found that a lower operation temperature was good for the depression of the hydrogen evolution from isolated catalysts, but would not change the BH_4^- electrooxidation mechanism. Like other fuel cells such as the PEMFC and DMFC, the cell performance decreased at lower temperature.

5. Conclusions

Hydrogen evolution during operation of the DBFC, resulted from borohydride electrooxidation and borohydride hydrolysis from isolated catalysts. Hydrogen evolution can be effectively depressed by decreasing the amount of isolated catalyst, lowering the BH_4^- concentration on catalyst surfaces and finding catalysts where a quasi-8e-reaction can take place. Nafion addition to the anode depresses hydrogen evolution during operation by a decrease of the isolated catalysts and a regulation of the borohydride concentration on the catalyst surfaces. However,

adding too much Nafion to the anode degrades the DBFC performance.

The hydrogen evolution rate of the Ni anode can be decreased by addition of Pd, Ag and Au catalysts. Adding a carbon supported Pd with a suitable content of Nafion to the Ni anode, not only depressed the hydrogen evolution but also improved the DBFC performance. Ag or Au additions depressed the hydrogen evolution more effectively than Pd additions, but degraded the DBFC performance.

Low operation temperature was good for reducing hydrogen evolution with some penalty for cell performance.

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