

Short communication

Influences of fuel crossover on cathode performance in a micro borohydride fuel cell

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Abstract

Influences of borohydride crossover on cathode performance were studied in a micro direct borohydride fuel cell (DBFC). The results showed that fuel crossover resulted in decreases in open circuit potentials of cathodes. On the other hand, effects of fuel crossover on cathode overpotentials strongly depended on the cathode material. The Pt/C cathode demonstrated a small potential drop of 0.11 V, while the Ag/C cathode had a much larger potential drop of 0.26 V under the same condition. Fuel crossover was found to be depressed during current operations. It is possible that fuel depletion happened around the anode during operation, resulting in a decrease of fuel concentration gradient across the membrane and thus less crossover. Experiments also showed that a balance in wet-proof property is essential for the cathode in the direct borohydride fuel cell and the stability of cell performance was mainly dependent on wet-proof durability of the cathode.

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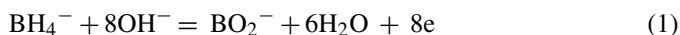
Keywords: Direct borohydride fuel cell; Fuel crossover; Cathode; Platinum; Silver

1. Introduction

Fuel cells are attracting more and more attentions as alternative power generation devices as they generate electricity with higher efficiency and lower pollution. Currently, proton exchange membrane fuel cells (PEMFCs) represent the most advanced fuel cell technology and are posing for mass production for vehicles and stationary applications. On the other side, direct methanol fuel cells (DMFCs), which adopt the structure of the PEMFC but use methanol instead of hydrogen as the fuel, are promising for portable applications to replace batteries. In principle, the DMFC system allows to be more compact and efficient than the PEMFC as it eliminates the necessity of fuel processing. However, practical performance of DMFC is inferior to that of the PEMFC due to low activity of methanol and its severe crossover to the cathode side. Methanol crossover not only lowers fuel utilization but also impairs cathode performance. Efforts have been devoted to decrease methanol crossover by limiting

methanol concentration, increasing operation temperature and current density or by membrane modification [1–3].

Recently, direct borohydride fuel cells have aroused considerable interests for their potential high energy densities [4–15]. The DBFC employs alkaline borohydride solutions as the anodic fuel. The anode reaction is supposed to be as follows:



Compared with the direct methanol fuel cell, the direct borohydride fuel cell demonstrated high open circuit voltage and good cell performance at low temperatures [4], and thus is very promising for portable applications. Current researches on DBFCs are mainly focused on the development of anode materials to depress hydrogen evolution from competitive hydrolysis reaction and to achieve higher fuel utilization efficiency. Only a few papers reported cathode performances [9–11]. Recently, Verma et al. [9] and Feng et al. [10] reported that MnO₂ is suitable for cathode material in the DBFC as it shows high catalytic activity towards oxygen reduction but no activity for the anode reactions including electrochemical oxidation and chemical hydrolysis of BH₄⁻ ions. However, a low open circuit voltage of 0.8 V observed in their DBFCs [10] suggests that effects of

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fuel on the MnO₂ cathode need to be further investigated. Until now, influences of fuel crossover on cathode and cell performance in DBFCs are not yet systematically studied. In this paper, we examined effects of fuel crossover on cathode performance as a part of effort to decrease overpotentials and improve cell performance for DBFCs.

2. Experimental details

The structure of the passive micro borohydride fuel cell has been described in our previous paper [11]. The membrane–electrode–assembly (MEA) was sandwiched by two stainless steel plates with slits for fuel and air. The active area of the MEA was 6 cm². A fuel reservoir of 30 ml was attached to one side of end plate in which a borohydride solution was kept. The cathode worked by air breathing without any auxiliary facilities. An Hg/HgO reference electrode was placed in the fuel reservoir and it was enveloped by a N117 Nafion membrane to separate its electrolyte from the fuel.

A porous nickel electrode was used as the anode. It was made by mixing fine Ni powder (type 210 from Inco Ltd.) with polytetrafluoroethylene (PTFE), filling the mixture into a porous nickel foam substrate and finally pressing into the sheet form. The Nafion membrane N117, N112 and N211 were used as the ion exchange membrane between the anode and the cathode. The Nafion membranes were pretreated successively by boiling in 3% H₂O₂ solution and de-ionized water for 1 h and then stored in the de-ionized water for use.

Cathodes were homemade or commercial products from E-Tek. Inc. The home-made cathodes were prepared as follows: The Pt or Ag catalyst supported on Vulcan XC-72 was added to a diluted PTFE solution to form an ink and then the ink was spread on a PTFE-treated Toray carbon paper TGP-H-060. After drying in air, the electrodes were then heated to 573 K under an argon atmosphere for 1 h to achieve wet-proof property. The catalyst loading was Pt 1 mg cm⁻² or Ag 1.6 mg cm⁻². The cathode catalysts were commercial products from E-Tek. Inc., in which 30% Pt or 20% Ag was supported on Vulcan XC-72. Commercial Pt/C cathodes from E-Tek. Inc. with different wet-proof properties were also used in this study.

The fuel was prepared by dissolving sodium borohydride (98%, Finnish Chemicals, Finland) in a 6 M sodium hydroxide solution. All fuel cell tests were carried out at room temperature around 298 K.

3. Results and discussion

On the cathode in the DBFC, oxygen is reduced according to the Eq. (2).



The reaction is the same as that in an alkaline fuel cell (AFC). It is well known that oxygen reduction reaction in an alkaline medium show better kinetics than that in an acidic one and activation loss at the cathode is generally less than that with an acid electrolyte [16]. Another advantage of alkaline medium is the

easiness in choosing electrode materials. Besides precious metal Pt that is necessary for fuel cells like PEMFCs and DMFCs, some materials like Ag or MnO₂ are possible as cathode catalysts. In principle, the cathode materials used in AFCs can also be applied to the DBFCs. However, some new requirements are demanded for the cathode in a DBFC. First, the cathode in a DBFC should be less sensitive to fuel crossover. Second, the cathode should have good water management ability, especially in a passive cell in which no forced flow of oxygen or air would help removing liquid formed during the operation. Third, the cathode should show a good stability in its catalytic and water management abilities without degradation even under influences of permeated fuel and reaction products.

In a previous paper, we reported the performances of a passive micro DBFC cell operating at ambient conditions using Pt and Ag cathodes [11]. Nafion membranes were employed in our DBFCs to separate the anode fuel from the cathode and also act as ion transport medium. In principle, Nafion membrane as a cation exchange membrane will not allow the transport of borohydride ion. However, crossover of borohydride was observed in our research and others [7,4], due to the porosity of the membrane. In this work, we tested effects of borohydride crossover on performance of the cathodes containing Pt and Ag catalysts. Their performances in DBFC were evaluated especially in terms of sensitivity to fuel crossover and water management stability.

3.1. Effects of fuel crossover

Although the Nafion membrane is supposed to prevent contact of the fuel from the cathode, an eventual separation was found to be impossible considering the porosity of the membrane and large concentration gradient of borohydride across the membrane. Borohydride ions are also driven to the cathode by internal electric field between the electrodes. As a result, borohydride would crossover to the cathode side by diffusion and migration. It was reported that the crossover rate of borohydride ion through Nafion 117 was $0.4 \times 10^{-6} \text{ mol cm}^{-2} \text{ S}^{-1}$ from a 30 wt% NaBH₄ in 6 M NaOH solution to a blank 6 M NaOH, though it was the lowest crossover value among the studied membranes [4].

The fuel crossover was found to influence cathode performance by lowering down the cathode potential. Fig. 1 shows changes of the cathode potential after the fuel was introduced into the fuel reservoir. The Pt/C cathode potential got stable at about +0.07 V versus Hg/HgO (+0.168 V versus NHE) when the fuel reservoir was filled with a 6 M NaOH solution. This value reflects the open circuit potential of the oxygen reduction reaction (2). The actual cathode potential was found to be lower than the theoretical value 0.401 V (versus NHE) of the oxygen reduction reaction (2). The difference is mainly caused by the activation loss of the cathode. When a fuel with 5 wt% NaBH₄ replaced the sodium hydroxide solution in the fuel reservoir, an abrupt decrease of the cathode potential was found, as illustrated in Fig. 1. The cathode potential decreased from +0.07 V versus Hg/HgO to -0.056 V versus Hg/HgO. This potential decrease is supposed to be originated from the borohydride crossover to the cathode. As Pt is also a good catalyst for the borohydride

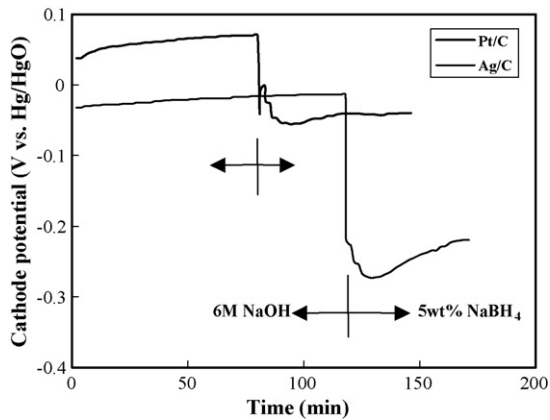


Fig. 1. Open circuit potentials for a Pt/C and an Ag/C cathode before and after the 6 M NaOH solution in the fuel reservoir was replaced by the 5 wt% NaBH₄-6 M NaOH solution (Pt/C cathode: Pt 1 mg cm⁻²; Ag/C cathode: Ag 1.6 mg cm⁻²; membrane: N112).

oxidation of Eq. (1), the crossover of borohydride led to a mixing potential of reactions (1) and (2), resulting in a shift of the open circuit potential to the negative side. However, the shift was not very large and the OCP was found to rise a little and became stable at about -0.04 V versus Hg/HgO. Hence, the overpotential originated from the fuel crossover in this experimental condition was about 0.11 V. This value is smaller than that in a DMFC caused by methanol crossover, which usually shows as high as 0.2 V when 1–2 M methanol was used [1].

On the other hand, the influence of fuel crossover on the Ag cathode was found to be much more significant than that on the Pt electrodes. As can be seen from Fig. 1, there was an abrupt decrease of 0.25 V after the fuel replaced the sodium hydroxide solution. Finally, the OCP got restored a little and became stable at -0.2 V versus Hg/HgO.

The large differences in OCPs shown by the Pt and Ag cathode can only be explained by their different reflections towards

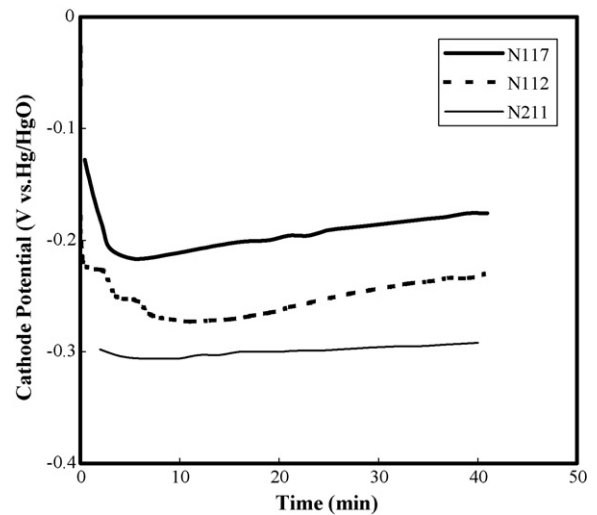


Fig. 2. Open circuit potentials for the Ag/C cathode changing with Nafion membrane thickness (fuel: 5 wt% NaBH₄ in 6 M NaOH; membrane thickness: N117 183 μm, N112 50.8 μm and N211 25.4 μm).

the fuel crossover. As the other parts in the cell were kept the same except the cathode, the initial crossover rate of borohydride across the membrane to the cathodes should be same no matter what the cathode material was. Therefore, the results shown above indicate that the Pt electrode was less influenced by borohydride crossover than the Ag electrode.

Two possible mechanisms may account for the different sensitivities of Pt and Ag towards fuel crossover. One explanation is that Pt is a good catalyst for borohydride oxidation while Ag is not as good as Pt. It is assumed that borohydride permeated to the cathode got oxidized on the cathode by a micro process combining reactions (1) and (2).

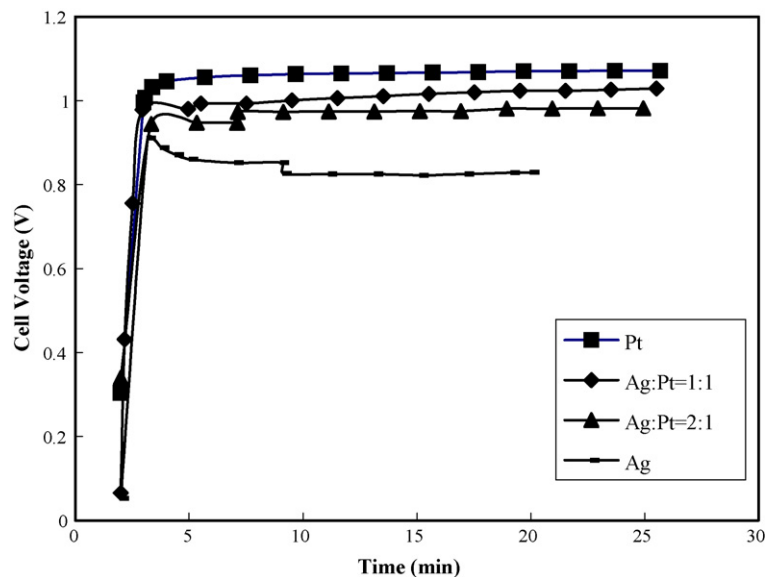
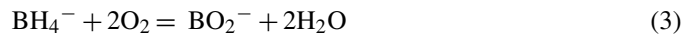


Fig. 3. Open circuit voltages of the cell changing with the cathode material: (1) Pt 1 mg cm⁻²; (2) Ag 0.7 mg cm⁻², Pt 0.7 mg cm⁻² (Ag:Pt = 1:1); (3) Ag 0.8 mg cm⁻², Pt 0.4 mg cm⁻² (Ag:Pt = 2:1); (4) Ag 1.6 mg cm⁻²; membrane: N112.

When borohydride permeates to the surface of the Pt cathode, it can be consumed by the reaction (3) under the catalysis of Pt. While on the Ag cathode, borohydride cannot be quickly consumed and thus its accumulation led to a much larger drop of OCP. Another possibility may be that Pt and Ag catalyst particles have different nature in water management ability. It is possible that Ag is more prone to be flooded by permeated borohydride, resulting in large potential drop.

The influence of borohydride crossover became more significant when the membrane became thinner. Fig. 2 shows that the thinner the membrane was, the lower the OCP became for the Ag electrode. As the fuel crossover rate is reversely proportional to membrane thickness according to the Fick's Law, there is no doubt that decrease of membrane thickness will greatly increase the crossover rate. Fig. 2 further suggests that the Ag electrode was strongly influenced by the fuel crossover.

Adding Pt catalyst in an Ag cathode can decrease the OCP drop caused by fuel crossover. Fig. 3 shows the variations of open circuit voltage with Pt contents in the cathodes. It can be seen that the higher the Pt content was, the higher the OCV of the cell became.

Borohydride crossover was found to be depressed under current operations. As shown in Fig. 4, the open circuit voltage of the cell became higher right after a current was drawn from the cell using the Ag cathode. Also, the larger the current was, the higher the OCV became. This phenomenon suggests that the effects of fuel crossover were alleviated due to the current. It was also reported that cell current led to significant decreases of methanol crossover in direct methanol fuel cells [2]. It was explained that a high current increases anodic consumption rate of methanol and then decreases concentration gradient of methanol across the membrane. In our case, two effects may account for the phenomenon shown in Fig. 4: a cell current may decrease borohydride permeation rate by decreasing borohydride concentration in the vicinity of the anode and thus lowers down the concentration gradient across the membrane. At the same time, the current also helps removal of permeated borohydride on the cathode by the flowing of liquid products. As

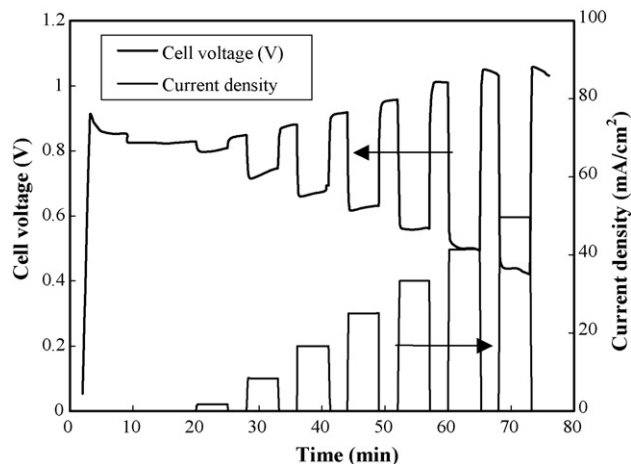


Fig. 4. Increases of the open circuit voltage after the currents were drawn from the cell (cathode Ag 1.6 mg cm^{-2} , membrane: N112).

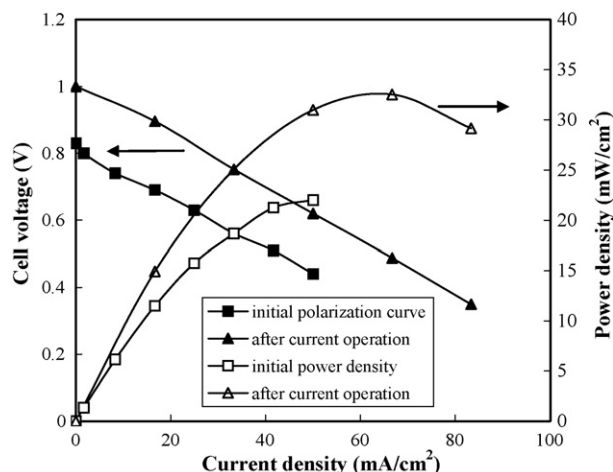


Fig. 5. Change of the polarization curve before and after the current operation (cathode: Ag 1.6 mg cm^{-2} ; membrane: N112).

described in our previous paper [11], NaOH solution would be produced on the cathode when a Nafion membrane is used. It can be imagined that a flux of NaOH solution with less borohydride permeation cleans the cathode surface and the surface concentration of borohydride would be decreased. This can explain that the OCV retained to a higher value after currents were drawn from the cell.

As the fuel crossover was alleviated at high currents, it can be expected that overpotentials caused by borohydride crossover would be decreased at higher currents. Therefore, the effect of fuel crossover on cell power density would not be very significant. Fig. 5 shows the comparison of polarization curve before and after the current operation of 50 mA cm^{-2} , 1 h for the cell using the Ag cathode. It can be seen that high current helped to reduce the overpotentials caused by borohydride crossover.

3.2. Water management

Another important property demanded for the cathode in DBFC is the water management ability. The cathode reaction shown as reaction (2) suggests that water is one of the reactants. Therefore, the cathode should have ability to hold sufficient water for the cathode reaction. On the other side, water in anode fuel will move with Na^+ under electro-osmotic drag to the cathode side. Therefore, the cathode should be able to remove the formed NaOH solution efficiently in case the liquid influences oxygen gas diffusion. Accordingly, the cathode should have a balance between the hydrophilic and hydrophobic properties. Experiments showed that a wet proof around 40% would be suitable for the DBFC cathode. As shown in Fig. 6, higher and lower wet-proof ability induced smaller limiting current.

3.3. Performance stability

It was reported that the cathode in DMFCs demonstrated early and high performance degradation compared with PEFCs. Knights et al. [17] reported that a DMFC operating for only 16 h under constant current load had lost significant performance at

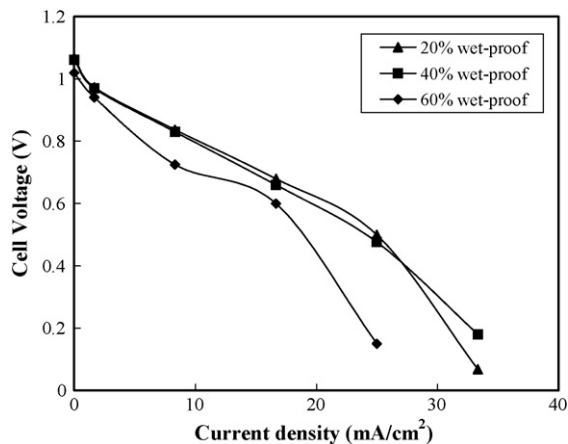


Fig. 6. Polarization curves for the cell using Pt cathodes with different wet-proof levels (cathode: Pt 1 mg cm^{-2} from E-Tek. Inc.; membrane: N117).

high current densities due to mass transfer losses caused by gas diffusion limitations. It was pointed out that the DMFC is prone to cathode flooding because a significant portion of the water in the fuel crossovers to the cathode and results in increased mass transfer losses. They also found that the cathode performance degradation could be greatly reduced by a load cycling strategy in which the load was removed from the cell for 30 s during every 30 min operational period.

As liquid NaOH solution is formed in the DBFC using the Nafion membrane, the working condition makes the cathode easier to suffer from flooding and performance degradation. Fig. 7 demonstrated the decreases in power density with operation hour. The cell was tested under a current density of 50 mA cm^{-2} and every 5 h the test was interrupted for renewing of the fuel. In Fig. 7, it can be seen that the cell with the Pt cathode showed gradual performance degradation, while the cell using an Ag cathode showed sudden loss of performance.

To explore reasons for performance deterioration of the Ag cathode, experiments were carried out to find if the deteriorated cathode could be recovered.

It was found that the cathode performance recovered after re-treating the electrode by heating at 300°C under argon atmosphere for 1 h, by which the electrode achieves wet-proof property. It suggests that the performance deterioration for the Ag cathode was caused by loss of its water management ability. Connecting this behavior with its high sensitivity towards borohydride crossover, it is very possible that the Ag electrode had poor property and stability in its water management ability compared with the Pt cathode. Further studies are undergoing to prove if the high sensitivity to fuel crossover and low performance stability are relevant for the Ag electrode.

4. Conclusions

A micro borohydride fuel cell was built up using a Nafion membrane to separate the fuel from the cathode. However, fuel crossover was observed and its influence on cathode performance was investigated in this work. It was found that the Pt/C showed a potential drop of about 0.11 V under the fuel crossover. On the other hand, the cathode using Ag/C catalyst demonstrated a potential drop of 0.26 V, much larger than that on the Pt cathode. Current operation was found to depress fuel crossover, possibly due to a decrease of fuel concentration gradient across the membrane caused by fuel depletion around the anode. Pt cathodes were also found to have better performance stability than Ag cathodes.

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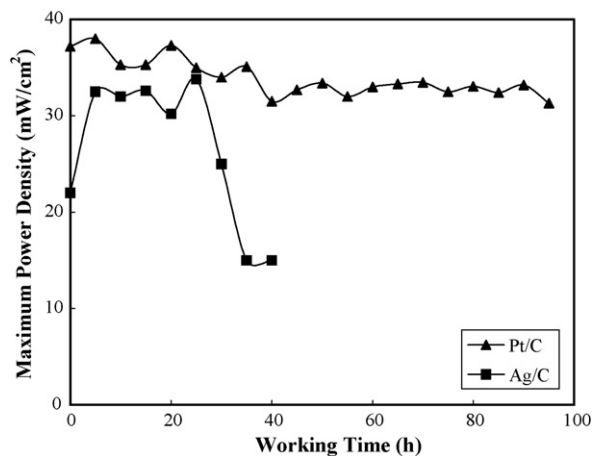


Fig. 7. Performance stability of the cell using Pt/C cathode or Ag/C cathode (Pt: 1 mg cm^{-2} ; Ag: 1.6 mg cm^{-2} ; membrane: N112; fuel: 5 wt%NaBH₄ in 6 M NaOH).