

Study of water-flooding behaviour in cathode channel of a transparent proton-exchange membrane fuel cell

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Abstract

The distribution of water and water flooding inside the cathode gas channels has been successfully visualized by using a transparent proton-exchange membrane fuel cell. The effect of various stoichiometries of cathode gas concentration and humidification are evaluated in a systematic way. The output voltage is controlled in the mass-transfer region (0.4–0.6 V) and the cell temperature is fixed at 50 °C. The cell performance increases with increasing stoichiometry of humidified oxygen until the stoichiometry reaches a critical value. On the other hand, the performance decreases with increasing stoichiometry of non-humidified oxygen. On replacing oxygen with humidified air, the cell performance and stoichiometry of the humidified air are in direct proportion due to the increasing mass-transfer rate.

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1. Introduction

In past decades, several efforts have been made for the integration of proton-exchange membrane fuel cells (PEMFCs) into terrestrial applications such as local power generation and zero-emission electric vehicles.

It is well known that the cathode of the PEMFC is the performance-limiting component due to the slow kinetics of oxygen reduction and the mass-transfer limitations imposed by the liquid water generated by the electrochemical reaction and electro-osmotic drag. The major obstacle that prevents a fuel cell from realizing its theoretical limiting current density is most probably a reduction in the effective porosity due to accumulation of liquid product water inside the flow channels, the gas-diffusion layer or the catalyst layer. Therefore, knowledge about the amount of liquid water inside the fuel cell is of great technical significance. Water management is one of the critical issues to be resolved in the design and operation of PEMFCs.

A theoretical study of the water-management problem in PEMFC anodes and cathodes has been reported by Okada et al. [1–3]. Their investigations revealed that the current density

and water penetration parameters are essential in determining the water content of membranes. The authors developed a new methodology to cope with the problem of performance degradation of membranes in PEMFCs by impurity ions. Water-transfer equations were solved in an analytical form, and the performance of the fuel cells in presence of impurities could be predicted by simple procedures. According to the studies, both the current density and the membrane thickness are vital parameters in the water management of the fuel-cell membranes, and the presence of impurity ions in the membrane can severely intensify the water-management problem. Localized contamination at the interface between the cathode and the membrane was found to be even more serious than uniform contamination of the membrane or localized contamination at the anode side.

Satija et al. [4] have developed a neutron imaging technique for testing and evaluating the water-management system of a fuel cell. The dataset was also analyzed to quantify the amount of water in the flow channels and the gas-diffusion layer. Natarajan and Nguye [5] observed some variations in the current density along the channel which were caused by changes in the oxygen concentration due to reaction and dilution that results from water evaporation. Operating parameters, such as high temperature, stoichiometries, and low inlet stream humidity facilitated better water removal by evaporation and gave rise to higher net current. Mench et al. [6] demonstrated an on-line gas chromatographic

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method which allowed discrete measurement of the content of water vapour up to a fully-saturated condition. This technique can be used for detail studies of water distribution and transfer in a PEMFC. In recent years, transparent fuel cells have been extensively used to visualize the flooding phenomena [7,8]. Images of water formed inside the cathode gas channels are analyzed to explain the water flooding.

A better understanding of mass- and heat-transfer problems is indispensable for the improvement and the optimization of the design of PEMFCs. The present work focuses on the investigation of water flooding in the cathode side of a PEMFC. A transparent fuel cell consisting of two serpentine channels is used for visual analysis. The voltage of fuel cell is controlled in mass-transfer region (0.4–0.6 V). The effect of various stoi-

chiometries on cathode gas concentration and humidification is examined. Images of water formed inside the cathode gas channels are presented to explain the phenomena of water flooding and membrane dehydration. The experimental results show that the stoichiometry of the cathode gas plays an important role in the performance and stability of fuel cell.

2. Experimental

A transparent fuel cell similar to the design of Yang et al. [9] was fabricated to investigate water flooding in a PEMFC. A schematic diagram of the cell is presented in Fig. 1(a). The membrane-electrode assembly (MEA, thickness between electrodes: 25 μm ; catalyst loading of anode and cathode: 0.1 and

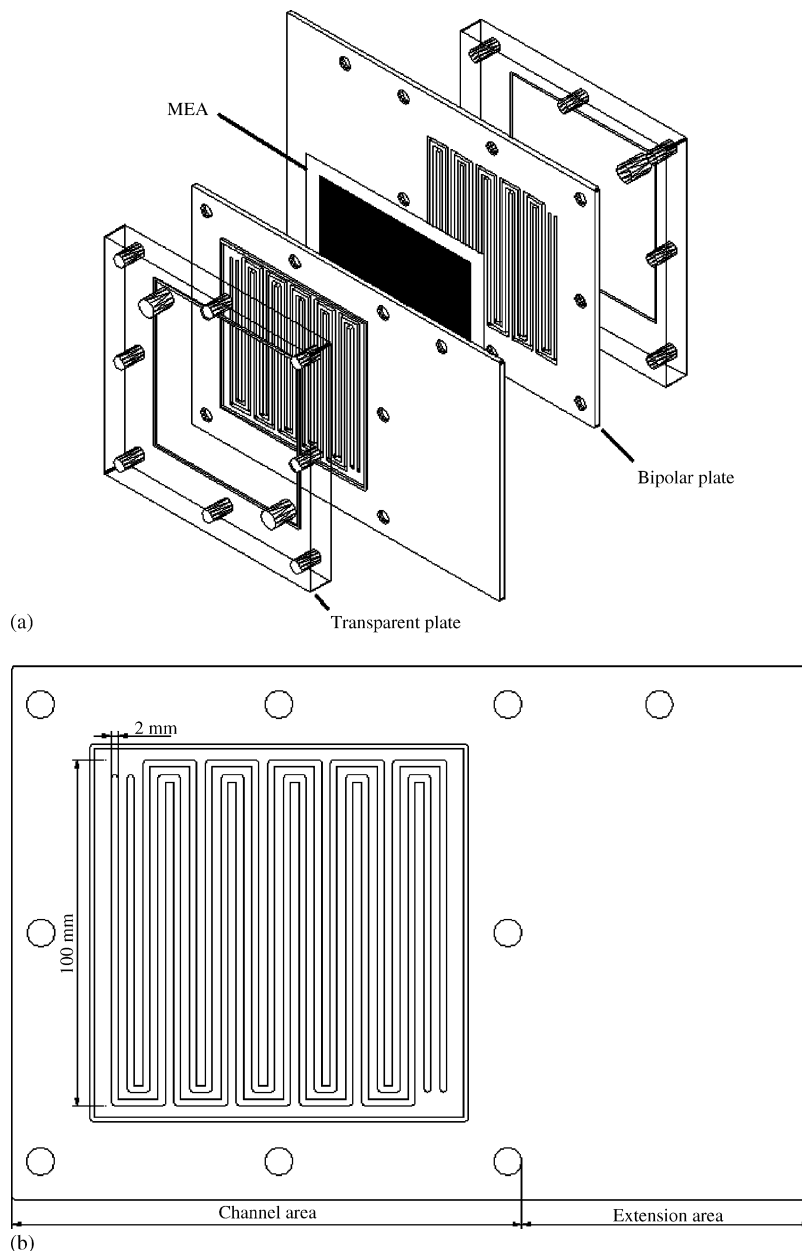


Fig. 1. (a) Schematic of transparent PEMFC; (b) schematic of bipolar plate.

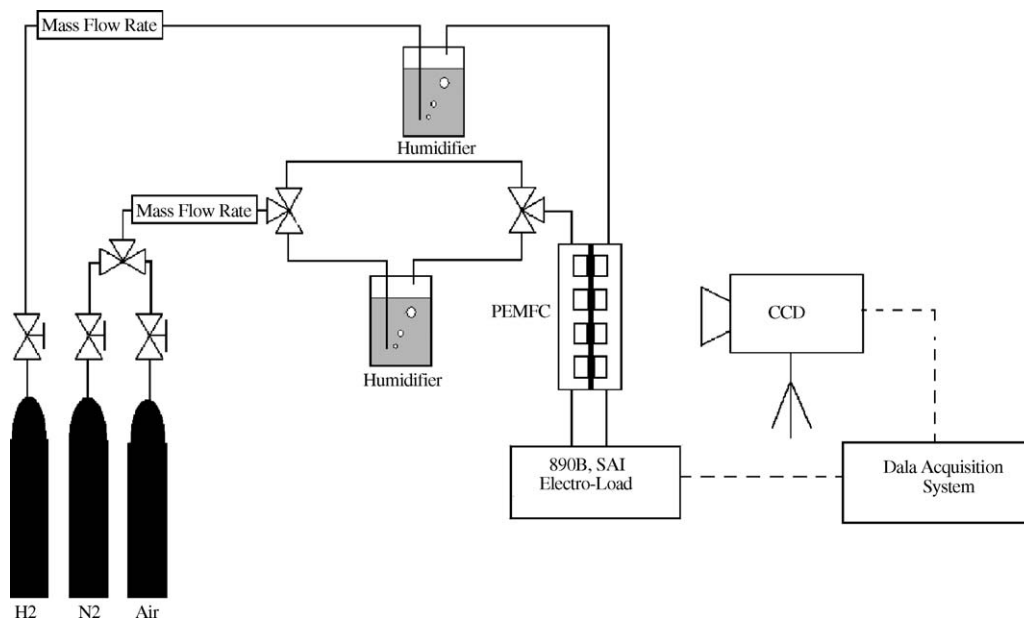


Fig. 2. Schematic of experimental equipment.

0.3 mg Pt cm⁻², respectively) is sandwiched between two bipolar plates, each of which has an active area of 100 mm × 100 mm. The PEMFC is clamped with eight screw joints that are tightened with a uniform torque of 50 kgf cm.

The bipolar plate of the fuel cell, which is placed between two transparent acrylic cover plates, is shown in Fig. 1(b). Two serpentine channels with a width of 2 mm and a depth of 2 mm are formed on the anode and cathode sides, i.e., the flow field on the anode side is the same as that on the cathode side. The extension area on a brass plate acts as a fin or heater. The extension areas become fins to reduce the temperature by free or forced air convection with the environment when the cell temperature becomes too high. When the temperature is too low, a heater is attached to the extension area to increase the cell temperature.

The experimental set-up, which is shown in Fig. 2, consists of gas-supply unit, a fuel cell, a close-circuit digital camera (CCD), an electronic load and a data acquisition system for analysis. The flow rates of air, oxygen and hydrogen are regulated by mass-flow controllers (Model #1179, MKS). All gases are humidified at 70 °C. The fuel cell is connected to an electric load (890B, SAI) that is operated in a constant-current discharge mode.

Flooding phenomena were observed at different current densities. Cathode gas stoichiometries of 2, 4, 6, 10 and 20 were used for each value of current density and the hydrogen stoichiometry was constant at 1.2. The cycle time of each experiment was 1 h for each cathode gas stoichiometry. During cycling, images at each second were taken by the CCD. All parameters such as current, voltage, fuel cell temperature and humidifier temperature were recorded with the data-acquisition system.

For every test, the MEA undergoes an activation process to ensure that the fuel cell has reached a stable status. The process involves running the fuel cell at: (i) 0.6 V for 15 min; (ii) 0.4 V for 14 min; (iii) open-circuit potential for 1 min. The cycle repeated several times until the MEA is in a stable state.

3. Results and discussion

The voltage is controlled between 0.4 and 0.6 V and the humidified gas temperature is fixed at 70 °C. The operating temperature of fuel cell is fixed at 50 °C. According to the polarization, the fuel cell is in the mass-transfer region. In this region, the performance is affected by water flooding in the flow channel and water content in the MEA.

3.1. Case 1. Constant electronic load of 700 mA cm⁻² applied to a cell and with different stoichiometries of humidified oxygen

The power and resistance curves of various oxygen stoichiometries as a function of time is shown in Fig. 3(a) and (b), respectively. It can be seen that at stoichiometry of 2, the power and resistance of the cell are too unstable and are characterized by large and unsteady fluctuations. The fluctuation reduces as the stoichiometry increases. At this higher electronic load, a large concentration of H⁺ ions is required to keep the output voltage constant. It seems that an oxygen stoichiometry of 2 in cathode side gives insufficient humidification, which leads to the large fluctuation in output voltage. When the rate of gas flow increases, the output power also increases due to the increase in voltage. The output power reaches a constant level after a stoichiometry of 6, beyond that no change in output power is observed. The steady performance at stoichiometry of above 6 may be related to stable water content in the fuel cell.

The voltage fluctuation at constant electronic load of 700 mA cm⁻² with various oxygen stoichiometries is given in Fig. 4. Data were recorded at different stages of the process. The output voltage decreases for all stoichiometries after a certain period of operation. A relatively higher voltage is recorded after 6 h of operation and the fluctuation in voltage is also smaller at a

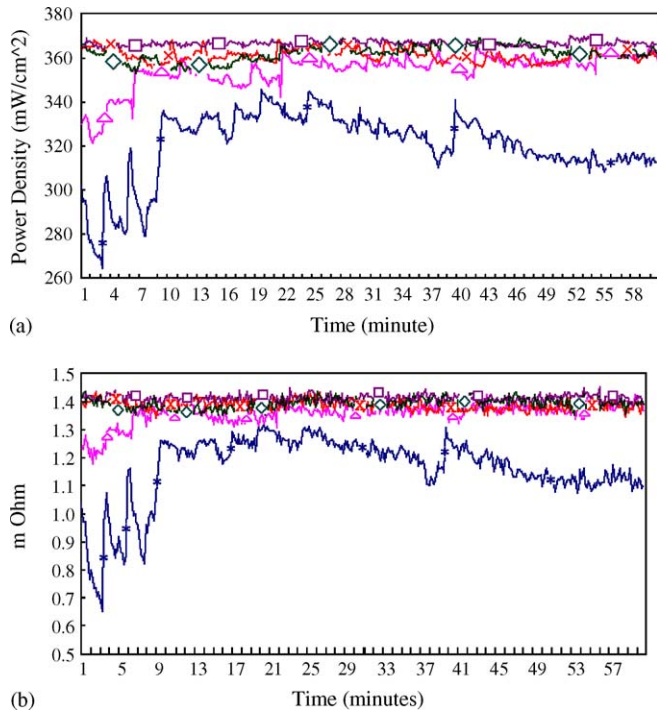


Fig. 3. Constant electronic load of 700 mA cm^{-2} , humidified oxygen with stoichiometry of: (*) 2; (Δ) 4; (\times) 6; (\diamond) 10; (\square) 20.

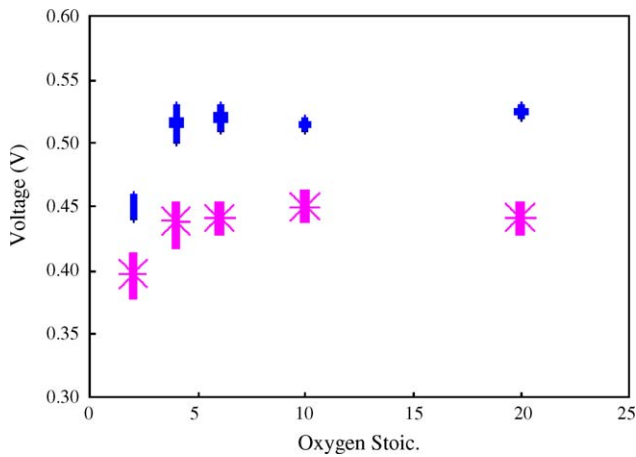


Fig. 4. Fluctuation of voltage after (■) 6 h and (*) 15 h at constant electronic load of 700 mA cm^{-2} .

stoichiometry of >10 . After 15 h of operation, however, the fluctuation in voltage becomes larger. In other words, the fluctuation of voltage is very small at high stoichiometry when the voltage is between 0.50 and 0.55 V. The liquid water is easy to remove at a large cathode gas stoichiometry (over 10 in present study); the membrane will not be dehydrated because of the humidified oxygen.

Voltage fluctuation increases when the value is between 0.35 and 0.45 V. This indicates that the cell performance is in an unsteady state. Thus, the voltage is lower when the current is higher, and the load of fuel cell is larger so that the output voltage becomes unsteady. On the other hand, a large current will cause an increase in the flow rate of the cathode gas.

As mentioned above, a large flow rate of cathode gas can remove liquid water in the flow channel. This will result in dehydration of the membrane. Water has a large influence in the mass-transfer region.

Images of the cathode side under operating conditions are presented in Fig. 5(a) and (b). It can be seen that the cathode channels are not clogged at an oxygen stoichiometry of 20. The status of the channels for stoichiometries of 2 and 20 are very similar. This explains why the cell performance is stable at higher stoichiometry. No channel flooding is observed under such operating conditions.

3.2. Case 2. Constant electronic load of 300 mA cm^{-2} applied to a cell and with different stoichiometries of humidified air

The power and resistance curves are shown in Fig. 6(a) and (b). As expected, the power increases with the stoichiometry. Nevertheless, the resistance of the cell for all stoichiometries is almost the same; the difference between the maximum and minimum resistance is only $0.3 \text{ m}\Omega$. This result suggests that the water content in the membrane is sufficient to carry stable operation. The fluctuation in the output power is also less than in case 1 discussed above. It appears that the effects associated with the water content required for normal operation are overwhelmed by those associated with the oxygen concentration required for the reaction. Compared with the pure oxygen condition, the limit of output performance becomes the concentration of oxygen due to the 21% of oxygen in air. The dilution of the oxygen concentra-

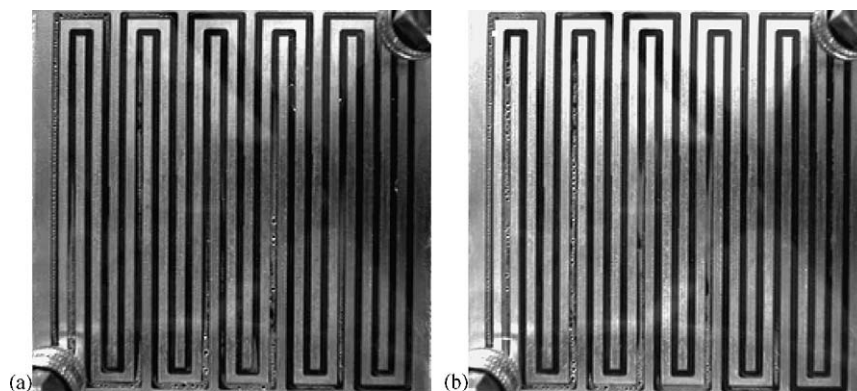


Fig. 5. Images of cathode gas-flow channels operating with humidified oxygen at constant electronic load of 700 mA cm^{-2} and a stoichiometry of (a) 2 and (b) 20.

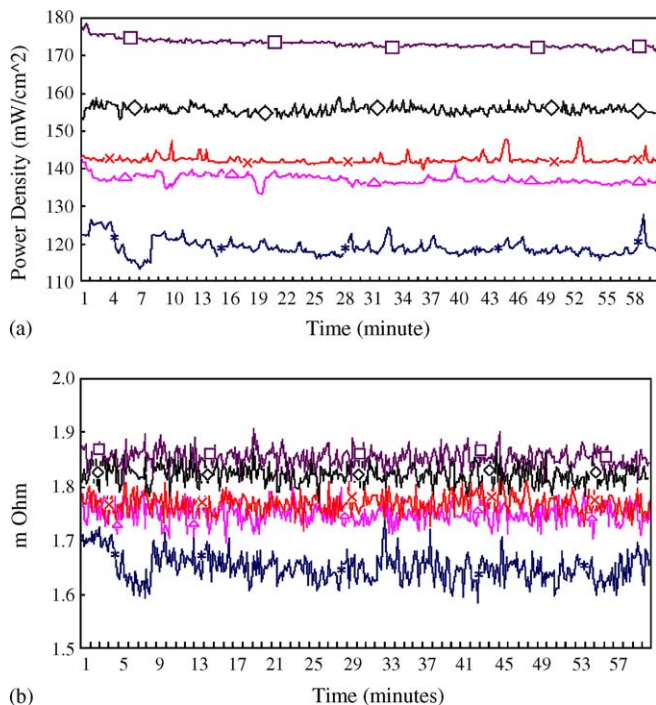


Fig. 6. Constant electronic load of 300 mA cm^{-2} , humidified air with a stoichiometry of: (*) 2; (Δ) 4; (\times) 6; (\diamond) 10; (\square) 20.

tion in air can be slowed down by increasing the stoichiometry of the air and thus the amount of oxygen required for reaction in the fuel cell will be increased. This will raise the output voltage. In addition, the flow rate of air must be higher than that of pure oxygen to achieve the same output voltage at constant current due to the presence of nitrogen in air. The vapour carried by nitrogen can support the reaction in the fuel cell. The liquid water can be removed by large stoichiometry (e.g. 20) and the amount of vapour in the air can support the cell reaction in the mass-transfer region.

When the stoichiometry of air increases, the oxygen consumption by the fuel cell also increases and this increases the output power. The effect of air stoichiometry on output voltage is demonstrated in Fig. 7. The plot reveals two regimes of operation, devoted by section I and section II, that depend on the air stoichiometry. Section I corresponds to stoichiometry of <15 , whereas section II represents operation of an air stoichiometry

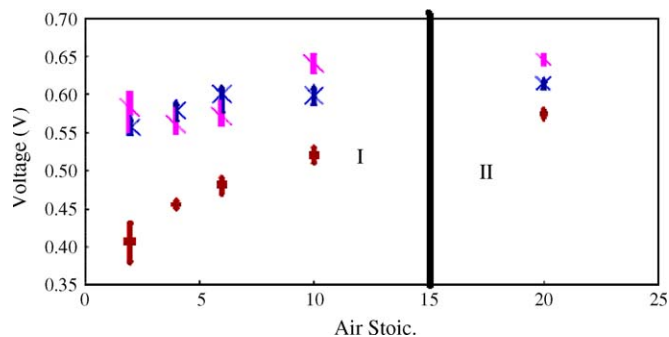


Fig. 7. Fluctuation of voltage at constant electronic load of (\circ) 30 , (\times) 100 and (\blacksquare) 300 mA cm^{-2} .

>15 . It is found that the output voltage of the fuel cell increases with the stoichiometry of the humidified air in section I. The fluctuation in voltage in section I is larger than that in section II. This is due to the effect of the concentration of oxygen in air. The state of the fuel cell is better in section II. In contrast to the previous case, at a stoichiometry of 2, some of the cathode flow channels are flooded by water, as shown in Fig. 8(a). On the other hand, liquid water is pushed along the flow channels at an air stoichiometry of 20 (Fig. 8(b)). These results suggest that it is better to operate the fuel cell with humidified air at a stoichiometry above 15.

3.3. Case 3. Constant electronic load of 300 mA cm^{-2} applied to a cell and with different stoichiometries of non-humidified oxygen

This case examines the effect of non-humidified oxygen. The power curve at different stoichiometries is shown in Fig. 9(a). The data shows that the behaviour is the reverse of that in cases 1 and 2 above, i.e., the cell performance deteriorates when the stoichiometry of the cathode gas increases. The resistance of the cell measured for all stoichiometries less than 20 are steady, as shown in Fig. 9(b). It is known that a large gas flow rate can remove too much water by dehydrating the membrane so that the resistance becomes unsteady. The fluctuation in output power at a stoichiometry of 20 becomes severe due to an insufficient water content in the membrane.

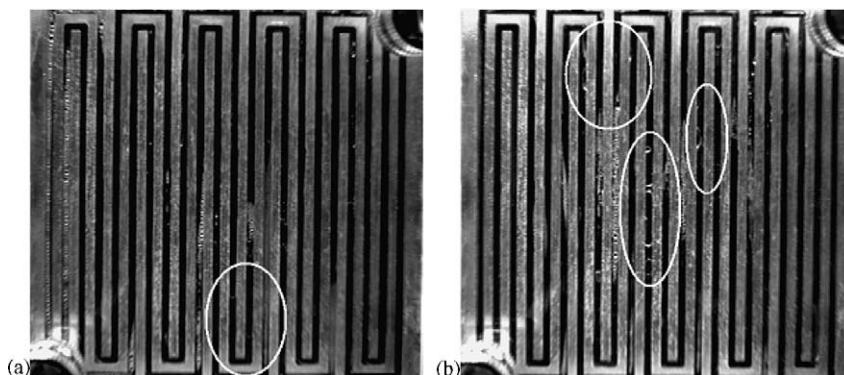


Fig. 8. Images of cathode gas flow channels operating with humidified air at constant electronic load of 300 mA cm^{-2} and a stoichiometry of (a) 2 and (b) 20.

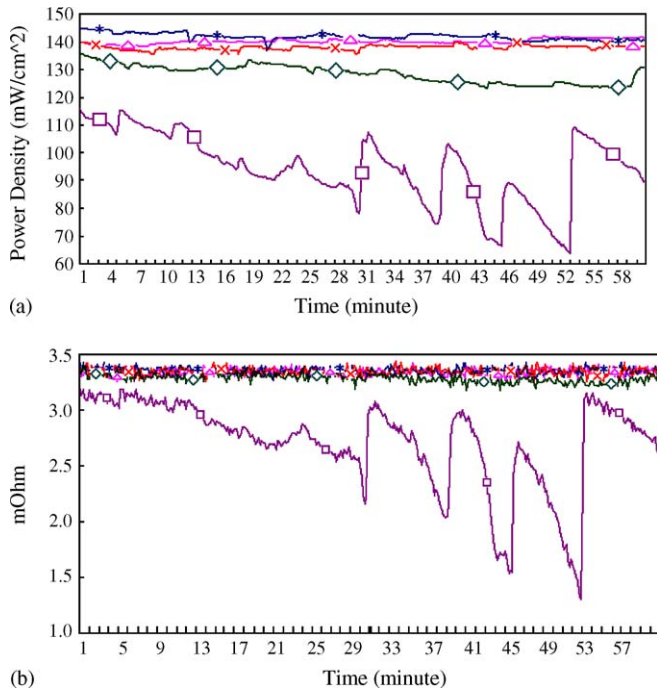


Fig. 9. A constant electronic load of 300 mA cm^{-2} , non-humidified oxygen with a stoichiometry of: (*) 2; (Δ) 4; (\times) 6; (\diamond) 10; (\square) 20.

The fluctuation in voltage is shown in Fig. 10 and is divided into two sections. In section I, the output voltage is steady and its fluctuation is smaller than in section II. As the cathode oxygen is not humidified before entering the fuel cell, the vapour in the oxygen is insignificant. The cathode gas can remove some of the water in the channels at lower stoichiometry, but still some water remains. Under these conditions, the output voltage is around 0.45 V where the effect of mass-transfer is not obvious. Thus, a lower amount of water is required for stable operation. These factors lead to a better output voltage, as shown in section I of Fig. 10. The output voltage in section II is lower than 0.45 V, which corresponds to a region dominated by mass-transfer. The liquid water is removed by the large stoichiometry and as a result, the membrane is dehydrated easily due to dry cathode gas. This suppresses the output voltage and sometimes even shuts down the system. (With a current load of 50 A no data a stoichiometry

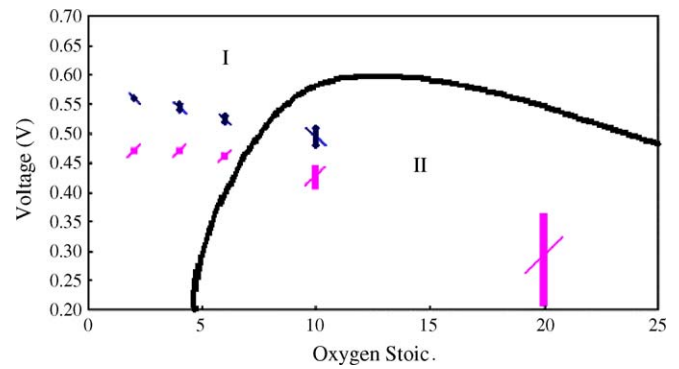


Fig. 10. Fluctuation of voltage at constant electronic load of (*) 500 and (x) 300 mA cm^{-2} .

of 20 is recorded for that reason). The output voltage is better in section I than in section II under the condition of non-humidified oxygen, as shown in Fig. 10.

Images of the cathode side under operating conditions are presented in Fig. 11(a) and (b). Water flooding is obvious at the bottom of the image at a stoichiometry of 2, which disappears at stoichiometry of 20. As described above, the membrane is dehydrated due to the large stoichiometry of non-humidified gas. This is why the output voltage is unsteady and decays at large stoichiometry.

3.4. Fluctuation of voltage on effect of concentration and humidification at different cathode gas stoichiometries

The effect of concentration and humidification on fuel cell performance for three different conditions (humidified oxygen at 70°C , humidified air at 70°C and non-humidified oxygen) is shown in Fig. 12. The current is constant in each experiment, so that the increase in voltage indicates better cell performance. The behaviour for all conditions is similar when the stoichiometry is below 10. This is because the ability of cathode gas to remove water is low at small stoichiometry. Thus, there is still some water in the MEA to support the reaction. According to this result, the effect of water removal has little influence on the performance of the fuel cell at a certain stoichiometry (a value of 10 in the present study). The output voltage of the humidified

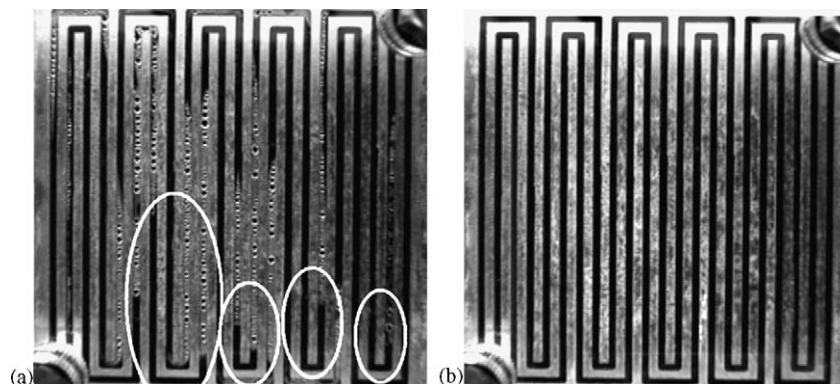


Fig. 11. Images of cathode gas-flow channels operating with non-humidified oxygen at constant electronic load of 300 mA cm^{-2} and a stoichiometry of (a) 2 and (b) 20.

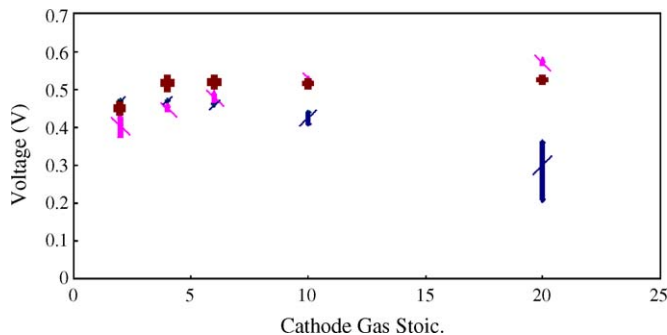


Fig. 12. Fluctuation of voltage for different conditions at constant electronic load of (∗) 300 mA cm^{-2} , humidified air; (□) 300 mA cm^{-2} , non-humidified oxygen; (■) 700 mA cm^{-2} , humidified oxygen.

oxygen is slightly higher than that of the other two conditions in Fig. 12. This reveals that at stoichiometries less than 10, control of parameters such as concentration and humidification is important to achieve better cell performance.

4. Conclusions

The present study reveals the effect of gas concentration and humidification at different stoichiometries in the cathode flow channels on the performance of a PEMFC. Images from a transparent cathode flow channel are observed at different operating conditions to understand the effects of concentration and humidification on cell performance. The findings are as follows:

- (1) A larger stoichiometry has a beneficial effect on the performance of the fuel cell under humidified conditions. Liquid water is easily removed at a high cathode gas flow rate and the reaction is not hindered by flooding. The vapour in the

cathode gas can support the mass-transfer reaction in the fuel cell.

- (2) The membrane will dehydrate and the cell resistance will increase due to a large stoichiometry when the cathode gas is non-humidified. Under these conditions, the cell performance is unsteady.
- (3) The output power reaches a maximum at some stoichiometry when it is operated with pure oxygen.
- (4) With air, the limiting factor is oxygen concentration. Thus, the fuel cell can use more oxygen at a larger stoichiometry and the output power will increase as the stoichiometry increases.
- (5) The effect of humidification on the fuel cell performance is similar irrespective of any other conditions, when the cathode gas stoichiometry is below a certain value, i.e., 10 in present study. On the other hand, humidification exerts a large influence when the stoichiometry is above 10. The membrane dehydrates under non-humidified conditions and, as a result, the output voltage decays.

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