Study on self-humidified PEMFC with reactant circulation

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Abstract

New stack for proton exchange membrane fuel cells (PEMFCs) has been developed to improve the performance of PEMFCs under non-humidifying condition by supplying reactant in series. The electromagnetic pump was used in the circulation pipeline to enhance the flow rate of reactants and thus to reduce the uneven distribution of water. Performance of the new stack was studied by using polarization curves and constant current test under various conditions.

Keywords: Self-humidification; Reactant circulation; Exhaust; Flow rate; Water distribution

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered to be one of the most attractive power sources for portable application. Polymer electrolyte membranes (PEMs) used for PEMFCs require water to maintain proton conductivity. The maximum degree of hydration of the membrane electrolyte is vital for the PEMFCs to attain its highest performance, but the more water might flood catalyst layer and block diffusion layer.

Up to now, several methods have been proposed to obtain self-humidification and water management. Thinner electrolyte films were introduced to increase the diffusion of water from cathode to anode [1–4]; Pt-layer was sandwiched into membrane to catalyze the production of water from crossover flux of H2 and O2 across the membrane [5–11]; hydrophilic SiO2 was embedded into the membrane to preserve water [12,13]. These methods, however, still cannot eliminate the uneven distribution of water in stack. The water content at the inlet region of stack is lower and increases along the channel, the different cells in the same stack present uneven water content too [14,15].

In order for the stack to be operated without humidification, they should have capabilities to preserve product water and distribute water evenly. In this context, we are addressing the new “ladder” design of stack. Both the electron-connect and reactant supply were in series. The electromagnetic pump in the circulation pipeline enhances the flow rate of reactant. The water perverse and distribution capabilities of the stack were dependent on its exhaust amount and circulation flow rate of reactant.

In this work, we have investigated the effect of the circulation flow rate and exhaust amount of reactant on the performance of PEMFCs without humidification.

2. Experimental

2.1. Ladder design of the stack

The stack in our experiment consisted of three cells. The electro-connect was in series as well as reactant supply. The schematic view of the stack was shown in Fig. 1.

Single-face flow channels were machined onto the first and the forth graphite plates. The flow field on both sides of either the second or the third graphite plates was interlaced. The flow field above the second plate contacted with the anode of #1 cell, the below flow field of the second plate contacted with the cathode of #2 cell, the flow field above the third plate contacted with the anode of #2 cell, the below flow field of the third plate contacted with #3 cell. Reactant was introduced into the stack at the inlet, passing through #1 cell, #2 cell and #3 cell in series. The flow field was machined as parallel channels design. In my research, the wider and short channels were chosen to avoid flooding. The length of the channel was 25 mm, the width of rids and channels were 2 mm. Area of every flow field was 7.5 cm².

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The path of reactant circulation was shown in Fig. 2. The flow rate of inlet ($F_{in}$), the flow rate of reactant circulation ($F_{cir}$) and the flow rate of exhaust ($F_{ex}$) were recorded. We also can see that $F_{in}$ equals to the sum of electrochemical reaction consumption and $F_{ex}$. $F_{cir}$ was adjusted by electromagnetic pump, and $F_{ex}$ can be adjusted by outlet valve.

2.2. Preparation of membrane electrodes assemblies

The membrane electrode assembly (MEA) was prepared by pressing the electrode/membrane/electrode sandwich (the active area of the electrode was 7.5 cm$^2$) at a pressure of 1 Mpa at $30 \degree C$ near the start-up temperature of stack, we chose $30 \degree C$ for Nafion 112. On the catalytically active surface of the Pt/C electrodes with a Pt loading of 1 mg/cm$^2$, polymer solution was impregnated by brushing to improve the electrochemical contact between the electrodes and the membrane.

2.3. Electrochemical measurements

The aim of my research work is to develop self-humidified PEMFC in the portable application. To avoid the latent danger to user under higher temperature, we restricted the lower working temperature of stack. The most severe flooding would occur at lower temperature due to the liquid water condensation. Since $30 \degree C$ near the start-up temperature of stack, we chose $30 \degree C$ as the lowest research temperature of my stack, and tested the efficiency of the new deign on solving the problem of flooding. If no special note, the circulation pipeline was hold 0.1 MPa. The stack was pre-conditioned by operating with low flow rate of the reactant gases for 12 h.

Fig. 2. Schematic view of circulation.

3. Results and discussion

To obtain a high performance, the problem of membrane drying out at the inlet region of stack as well as the problem of electrode flooding at the outlet region should be eliminated or at least reduced. In principle, it is possible to operate a stack with dry gases under certain conditions. However, during the operation of a stack with relatively large active area, the water content is not evenly distributed. The inlet region of stack operating with dry gases presents lower water content. As for the outlet region, the reactant could be saturated by the product water and the problem of electrode flooding may occur.

To solve the problems mentioned above, ladder design was developed to supply gases in series and reactant circulation was used to improve the water distribution in the stack. Part of exhaust gas was led into the stack again after mixing with fresh gases (Fig. 2). Electromagnetic pump was assembled in the circulation pipeline to control the flow rate of reactants. Circulation can save reactants and carry water from the outlet to the inlet to humidify the fresh dry gas effectively. To avoid the water congregating in the last cells of stack, high speed circulation was executed and the wider channels with the width of 2 mm was used.

Two vital factors in the stack have to be considered, flow rate of exhaust ($F_{ex}$) and flow rate of circulation ($F_{cir}$). $F_{ex}$ means the amount of water removed from stack, overmuch water removal will lead to dehydration of membrane, insufficient water removal could induce electrode flooding. The water distribution extent is controlled by $F_{cir}$. Both $F_{ex}$ and $F_{cir}$ control the humidification of the reactant entering stack, which will decrease with $F_{ex}$ increasing and increase linearly with $F_{cir}$.

3.1. Influence of exhaust oxygen/air

The product water at cathode is the only water source of PEMFCs under non-humidifying condition. One part water of cathode diffuses to anode, one part preserves at cathode, another part is carried out by reactant gas. The influence of exhaust oxygen/air to remove water from the stack was further confirmed by the results shown in Figs. 3 and 4. Fig. 3 shows the effect of exhaust oxygen on the stack performance. We used $F_{in}$ to behave $F_{ex}$ (the consumption of electrochemical reaction at various current conditions was different, and the $F_{in}$ equaled to the sum of consumption and $F_{ex}$). The anode outlet valve was closed down. The circulation flow rate of the anode hydrogen and the cathode oxygen were kept 100 ml/min, and the pressures were held 0.1 MPa. The stack was pre-conditioned by operating under 133 mA/cm$^2$ for 30 min. The cell potential was averaged over 300 s after the current changed.

The performance of each cell improved with the oxygen exhaust increasing especially under higher current density. The excellent performance of #1 cell and #2 cell presented when the $F_{in}$ of oxygen was 80 ml/min, but 90 ml/min for #3 cell. The influence of oxygen exhaust on various cells was different due to the different location of each cell. It is also shown in Fig. 3 that the severe flooding at the end of stack. When the $F_{in}$ was 30 ml/min, nearing the entrance, #1 cell brought
out 186 mA/cm$^2$ at the terminal voltage of 0.2 V, while #2 cell and #3 cell brought out only 173 and 146 mA/cm$^2$; when the $F_{in}$ increased to 80 ml/min, the current of #1 cell increased to 333, 266 mA/cm$^2$ for #2 cell and 320 mA/cm$^2$ for #3 cell at the terminal voltage of 0.2 V. The $F_{in}$ increased from 30 to 80 ml/min, various improvements presented on the three cells of the stack.

Fig. 4 shows the performance of each cell improved with the air exhaust increasing. We chose the $F_{cir}$ of air as 400 ml/min, the operation conditions of anode were the same as in Fig. 3. The best performance of the three cells all presented when the $F_{in}$ of air was 300 ml/min. Two factors affected the performance of the three cells, water content and oxygen concentration. The design of supplying air in series made water content increase and oxygen concentration decrease from #1 cell to #3 cell, so the water content was the lowest and the oxygen concentration was the highest in #1 cell, and the contrary condition presented in #3 cell. We can see from Fig. 3 that when the $F_{in}$ was over 150 ml/min, no flooding would occur in the stack. When the $F_{in}$ was 150 ml/min, #1 cell brought out 186 mA/cm$^2$ at the terminal voltage of 0.2 V, while #2 cell and #3 cell brought out only 173 and 133 mA/cm$^2$; when the $F_{in}$ increased to 300 ml/min, the current of #1 cell increased to 213, 213 mA/cm$^2$ for #2 cell and 200 mA/cm$^2$ for #3 cell at the terminal voltage of 0.2 V. As the $F_{in}$ of air increased, the water content dropped, which increased the membrane resistance, but the oxygen concentration increased. The results show that the oxygen concentration had more effect on the performances of the stack than that of the water content.

Fig. 5 shows the constant current performances of the new stack at 133 mA/cm$^2$ operating with oxygen. The circulation flow rate of hydrogen and oxygen was kept at 100 ml/min, the hydrogen outlet valve was closed down and the inlet flow rate of oxygen was restricted at 70 ml/min, the consumption of oxygen was 10.5 ml/min, so the flow rate of exhaust oxygen was 59.5 ml/min. #1 cell, the nearest one to the entrance, the voltage dropped 0.07 V in 24 h, #2 cell, at the middle of the stack, the voltage dropped 0.1 V, the water had accelerated in #2 cell; #3 cell, near the exit, the voltage dropped 0.14 V, severe flooding occurred. When the oxygen inlet amount increased to 80 ml/min, the voltage decline of #1 cell was 0.21, 0.14 V for #2, only 0.05 V for #3, which indicated that, the flooding in #3 cell had been reduced, but the dehydration occurred in #1 and #2 cells. Suppose that, reactant has been fully saturated at outlet of stack, 70 ml/min of $F_{in}$ means 30% relative humidification at the inlet region, 80 ml/min of $F_{in}$ means 20% relative humidification at the inlet region. The results show that the relative humidification of inlet reactant is between 20% and 30%, which can be fully saturated in the stack.

Fig. 6 shows the constant current performances of the new stack at 133 mA/cm$^2$ operating with air. The circulation flow rate of hydrogen was kept at 100 ml/min, and the circulation flow
rate of air was kept at 400 ml/min, the hydrogen outlet valve was closed down and the inlet flow rate of air was chosen at 150 and 300 ml/min. Compared with Fig. 5, we can see that the amount of exhaust air in Fig. 6 was much more than the exhaust amount of oxygen, no flooding would occur. Fig. 6 shows that the voltage of the three cells all decrease in the initial period and stabilized in the following time, which indicated that, the cells can operate stably at the condition of shortage of water. The increasing amount of air inlet increased the resistance of membrane, but enhanced the oxygen concentration. The 50 mV drop of #1 cell, #3 cell and 25 mV drop of #2 presented in the two figures (a) and (b) of Fig. 6 indicated that the increased resistance of membrane had more effect on the constant current performances of the stack under the current density of 133 mA/cm².
3.2. Influence of exhaust hydrogen

Fig. 7 shows the effect of hydrogen exhaust on the performance of the new stack. Just like the above study on exhaust oxygen, we use the inlet flow rate of hydrogen to behave the exhaust hydrogen. We kept the inlet flow rate of oxygen at 45 ml/min, the circulation flow rate of hydrogen and oxygen at 100 ml/min. The inlet flow rate of hydrogen was adjusted.

Result shows that the exhaust amount of hydrogen has no obvious effect on the performance of the new stack. When the current density was under 133 mA/cm² and the exhaust of hydrogen increased to 100 ml/min, there was tiny decrease on the performance of #1 cell, but no considerable change occurred on #2 cell and #3 cell, which indicated that the reactant from #1 cell carried water and humidified the following cells to a certain extent. When the current density was above 200 mA/cm², some
change can be seen from the curves, especially the hydrogen inlet increased to 100 ml/min, which indicated that the flooding might occur under the condition of higher current density and low exhaust.

3.3. Influence of oxygen/air circulation

Fig. 8 shows the effect of the oxygen circulation. The inlet flow rate of oxygen was kept at 60 ml/min, the circulation flow rate of hydrogen was held at 100 ml/min, the anode outlet valve was shut down. The circulation flow rate of oxygen was adjusted by electromagnetic pump.

The results in Fig. 8(a)–(c) show the effect of the circulation flow rate of oxygen. When the $F_{\text{circ,c}}$ was 60 ml/min, almost all the tail gas of oxygen was exhaust out of stack, and the oxygen entering the stack was fully dry. The voltage of #1 cell dropped 0.336 V in 2 h, 0.395 V for #2 cell in 3 h, and 0.376 V for #3 cell in 1.5 h. The poor performance of the cells was induced by the uneven distribution of water content. When the $F_{\text{circ,c}}$ increased to 110 ml/min, the relative humidification of the inlet oxygen was 45%, the performance of the cells was significantly improved.

When the $F_{\text{circ,c}}$ exceeded 160 ml/min, the relative humidification of inlet oxygen was over 62.5%, the voltage became stably. Fig. 8(d) was the voltage after the stack operating 2 h at 133 mA/cm² and the inlet flow rate of oxygen was altered in the region of 130–180 ml/min. When the circulation flow rate of oxygen exceeded 160, there was no obvious change occur. Under 160 ml/min, the circulation flow rate of oxygen was not enough to distribute water evenly, the water might accumulate and block the catalyst layer.

Fig. 9. Cells potential vs. time plots for different cells at a constant current density of 133 mA/cm² ($T_{\text{stack}} = 30^\circ\text{C}$, $T_{\text{circ}} = 33^\circ\text{C}$, $p_a = p_c = 0.1$ MPa, $F_{\text{ex,a}} = 0$, $F_{\text{cir,a}} = 100$ ml/min, $F_{\text{cir,c}} = 500$ ml/min, the solid points obtained with $F_{\text{in,c}} = 150$ ml/min, and the hollow points obtained from Fig. 6 with $F_{\text{in,c}} = 300$ ml/min).
Fig. 10 shows the effect of the circulation flow rate of hydrogen. The inlet flow rate of oxygen was kept at 60 ml/min, circulation flow rate of hydrogen was held at 160 ml/min, the anode outlet valve was shut down. We adjusted the circulation flow rate of hydrogen was kept at 30 ml/min. The circulation flow rate of hydrogen was adjusted by electromagnetic pump.

4. Conclusion

The performance of the new stack has been investigated under various operating conditions. Ladder design was developed to supply gases in series, circulation was used to uniform the water distribution in stack. The combination of circulation and exhaust was used to adjust the humidification of the gases entering the stack. The experiments show that the operating condition change of oxygen/air has more effect on the performance of stack than that of hydrogen. As for the new ladder design of stack, water accumulation can occur when the stack operated with oxygen, which due to the insufficient removal. As the exhaust amount of tail gas increased, the flooding in stack can be avoided just as the stack operating with air.

We can also see from Figs. 5, 6 and 8–10, once the water balance was built, the voltage can be stable in a little voltage region. But this stability on different cells attained under different condition as for different cells. This is because the different
location of the cells, the reactant entering #1 cell has less water content than that entering the following cells. This reminded us to modify the cells design in different location of the stack to accommodate the different condition in the stack.

References