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Experimental Study of the Start-Up Process of Hydrogen-Oxygen PEMFC Stack With Dead-Ended Anode and Recirculation Cathode#

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ABSTRACT

The transient response of proton exchange membrane fuel cell (PEMFC) during start-up is an important issue for a system. In this paper, the start-up process of the 6-cell stack with the dead-end anode and recirculation cathode is studied. The effects of starting load, step size on voltage variation are studied via the measurement of time evolution of the stack voltage. In addition, the different start-up responses of the single-cell under the flow-through and recirculation are compared. It is found that increasing the start-up current density and reducing the step load change can shorten the start-up time. However, the shorter start-up time will result in the lower critical membrane dehydration temperature. Compared with the gas-through mode, when the stack with dead-end anode and cathode recirculation is started, the single cell near the outlet is more likely to be flooded at the moment of high current density start-up due to the closing of anode outlet.

Keywords: Proton exchange membrane fuel cell; Stack; Start-up; dead-end anode; cathode recirculation

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is considered an alternative energy source with great development prospects due to its high energy density, low operating temperature, and environmental friendliness[1]. At the same time, it is also attractive in the military field due to its low noise and low infrared signals, such as space and underwater vehicles. PEMFC operating in this closed environment often has its hydrogen and oxygen storage system and operates in pure hydrogen and oxygen working environment because it is isolated from ambient air[2]. At the same time, due to volume limitations, PEMFC systems are moving towards fewer components and higher efficiency. Therefore, most of the AUV PEMFC systems use the self-humidifying mode supplied directly with dry gas, because this way can eliminate the huge humidifier[3].

For PEMFC, researchers have done a lot of research on its water and heat management or any other different operating conditions under steady- [4-7]. In addition to conventional steady-state performance studies, various transient operating conditions, such as start-stop, variable load, variable flow, and temperature, which are closer to the actual operating conditions, are also understudies. Among them, the start and stop of PEMFC are unavoidable, therefore, many scholars have studied the starting characteristics of stack[8, 9]. It can be seen that the research on start-up conditions mainly focuses on the cold start-up of a stack below 0 ℃, which is indeed a difficult point to overcome for PEMFC. However, in addition to cold start under extreme conditions, a start-up at normal ambient or even higher temperature is unavoidable as the temperature of the cell will increase during operation. At this point, the cell should be able to start quickly in a short time after the load has been stopped to reach the required load conditions. Many scholars have studied the start-up at temperatures above 0℃ [10-12].

However, in practical applications, when pure hydrogen and pure oxygen are used, fuel cells are rarely straight through, because this will reduce gas utilization. Most are single-recirculation or double-recirculation arrangements[13].

This study is based on the arrangement of cathode recirculation and dead-end anode. Because the PEMFC stack is more suitable for constant current starting, the stack is started by a constant current step.

On this basis, the influence of starting current density and load step size on operating voltage is studied. The performances of flow through and single recirculation arrangements under different flow rates were compared. In addition, at the level of single cell, the influence of starting current density on the voltage of single cell is studied

2. EXPERIMENT

2.1 Fuel cell stack

The designed 300 W air-cooled proton exchange membrane fuel cell stack was tested. The stack consists of 6 single cells with a U-shaped inlet and outlet. The active area of each cell is 78 cm^2. The bipolar plates are made of graphite and the flow path is parallel serpentine. The electrocatalysts for both the anode and cathode are platinum with loads of 0.4 mg/cm^2 and 0.8 mg/cm^2 respectively. Table 1 lists the specific parameters of the stack.

Table.1. Design parameters of PEMFC stack

Parameters	*Values*	*Unit*
Active area	78	cm^2
Depth of flow channel	0.8	mm
width of flow channel	0.8	mm
Flow channel number	11	-
Cell numbers	6	-

The schematic diagram of the tested stack is shown in Fig. 1. The cell is operated with pure, dry hydrogen and oxygen. The inlet pressure of hydrogen and oxygen can be adjusted by a pressure relief valve. The flow rate is regulated by a flow meter. Due to the dead-end anode, a solenoid valve is installed in the hydrogen outlet to control purging. The cathode outlet is connected to a water-gas separator and circulating pump for oxygen recirculation. The stack is cooled by an external cooling fan. The experiment was carried out on a 5kW multifunctional fuel cell test rig, which controlled the supply of gas and load and ensured the safety of the experiment. These tests were performed in a constant current mode using an electronic load, recording stack and cell voltage data per second. Finally, real-time monitoring and storage of voltage, current, and temperature are realized on the computer by relevant software.

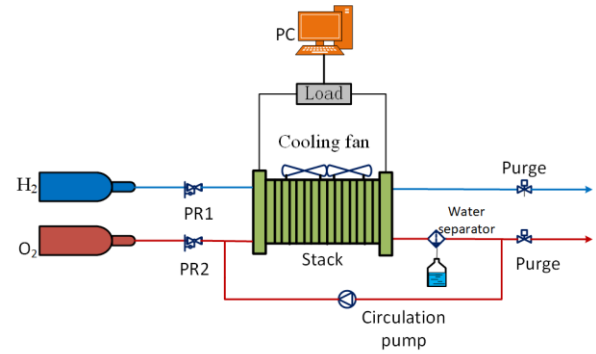

Fig.1. Schematic diagram of PEMFC stack of the dead-end anode and cathode recirculation

2.2 Experimental procedure

The start-up procedure consists of two consecutive stages as shown in Fig.2 First, feed dry nitrogen to purge the excess water inside the stack and provide a consistent initial condition for the stack. Then the intake valve opens and dried pure hydrogen and oxygen are introduced. The intake mode is counter flow. Gas flows in and out at ambient pressure when gas passes through, and the working pressure of the stack is set at 40 kPa when the anode is dead-end and the cathode is recirculated. Second, when the voltage stabilizes for 10 seconds at an open-circuit voltage, the fuel cell is connected to the load and a current step is applied. I_0 is the start-up current density. Current step size defined at P. Record the changes of stack voltage and single-cell voltage with time until a steady-state is reached. The time t from OCV to its stability voltage under the target load is defined as the start-up time.

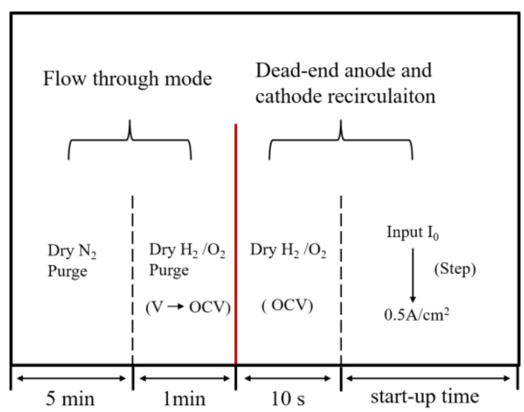

Fig.2. The procedure for dry gas start-up

3. RESULTS AND DISCUSSION

3.1 Stack basic performance

It is necessary to seek a working voltage point before the experiment. Underwater vehicles are more efficient than conventional power equipment such as trucks and automobiles because of the less frequent load changes and often work under stable operating conditions. Therefore, to improve efficiency, AUV often works at a single cell voltage at 0.7 to 0.8 V, so refer to Fig. 3 We take the current density of 0.5 A / cm^2 as the reference working current density. OCV in Fig. 4 shows that the voltage uniformity of the six cells is good without external circuit connections, which indicates that oxygen can reach each cell sufficiently.

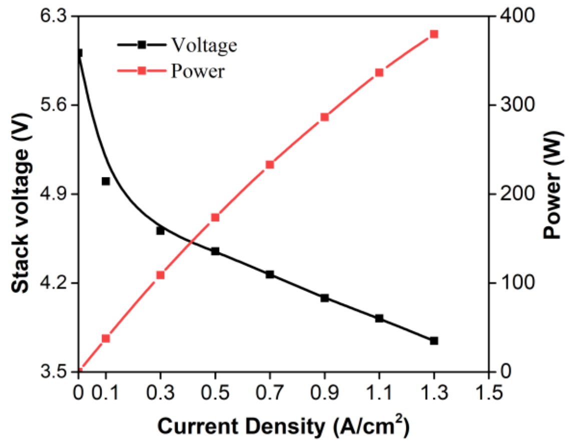

Fig.3. Voltage/Power-current curve for PEMFC stack.

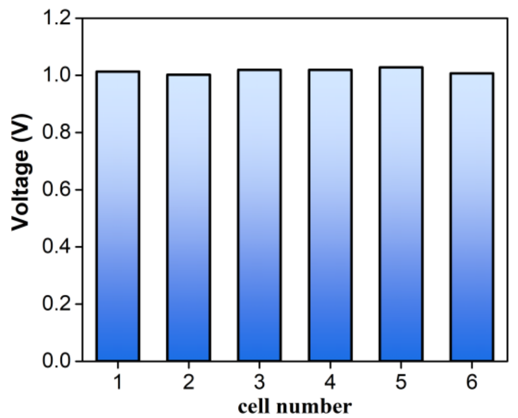

Fig.4. Voltage distribution of the PEMFC stack at OCV condition

3.2 Impact of step time

After the stack reaches its steady-state for 10 s at open-circuit voltage, it begins to give an initial starting current of I_0.

Fix the I_0 at 0.1 A and step the current until the working current reaches 0.5 A. Give current in step size p=10 s, 15 s, 30 s, and 60 s respectively to explore the start-up time and voltage changes when the target current is reached.

As shown in Fig.5a, when loading under different steps, the voltage when reaching the target load is basically the same, while the time to reach the target load obviously increases with the increase of steps. This shows that when the current changes to a given value, the stack can quickly reach the corresponding stable state in a few seconds. This is mainly since both the consumption of membrane water and the production of liquid water in the stack and the consumption and delivery of gas are all act at the moment of load changes and these actions can be completed in a few seconds. Therefore, the time step of more than 10 seconds or even tens of seconds is enough to make the stack reaches a basic voltage value. That means a shorter step size corresponds to a shorter start-up time without sacrificing the operating voltage.

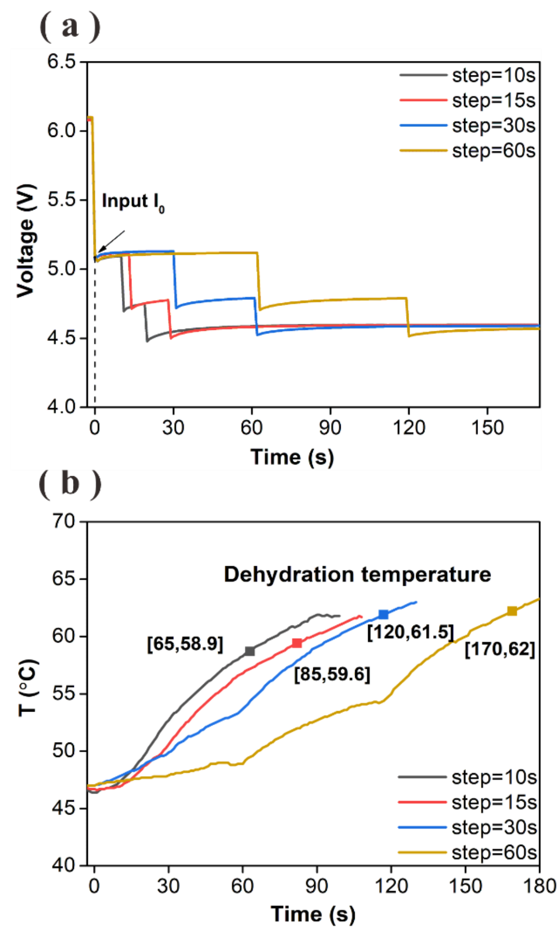

Fig.5. Voltage variations with time. (a) and temperature variations with time (b) for I_0 = 0.1A/cm^2 and fixed gases flow rates Influence of step.

Although the voltage at the target operating condition is basically the same, the stack temperature in the three steps is different when the voltage reaches a steady state.

Fig. 5b shows the time-dependent curve of stack temperature starting at different step sizes. It can be seen that a shorter step start-up method corresponds to a larger temperature growth rate. That is mainly because in the same amount of time, shorter step times produce more energy and more heat, so the temperature rises higher at the same temperature, the time required for a strategy with a small P is obviously higher than that of a large p-value. This also represents a higher heat release rate. Furthermore, the stack temperature corresponding to the voltage stability is marked with dots in the diagram. We refer to this dehydration temperature point as critical T_p, and it is interesting to note that although the voltages at the target operating conditions for the four strategies are basically the same, the stack temperatures differ when the voltages reach a steady state. As the step size increases, T_p moves toward higher temperatures. T_p divides the temperature curve into two parts. In the front part of T_p, the catalyst activity increases with the increase of temperature, so the reaction efficiency is improved. At this time, the temperature has a positive effect on the stack. When t is greater than T_p, the voltage is stable and the temperature has two opposite effects on the stack. First, the increase in temperature leads to the dehydration of the membrane, which hinders the transmission of ions, resulting in a decline in performance. On the other hand, the increase in temperature also continued to improve the activity of PEM, so the performance increased. Because of the counterbalance of these two opposing effects, the stack voltage remains essentially unchanged. Of course, it can be expected that if the temperature rises further, the voltage will decrease gradually as the rate of membrane dewatering is higher than the rate of temperature promotion. Therefore, when the T_p point is reached, appropriate cooling measures will be taken. Therefore, T_p represents the maximum temperature limit to which the stack should be cooled. Considering reducing the heat load of the radiator, a larger T_p is better.

3.3 Impact of I_0

Fix the step at 15s and step the current until the working current reaches 0.5 A. Give current from different I_0 respectively to explore the start-up time and voltage changes when the target current is reached.

As can be seen from Fig.6a, a higher initial current density has a shorter start-up time. Although the voltage of the stack decreases more at the moment when its load is at a large I_0, it does not affect the voltage when reaching the target power density. Therefore, in case the membrane is not completely dry, it is feasible to start with a large current directly and the starting time can be shortened.

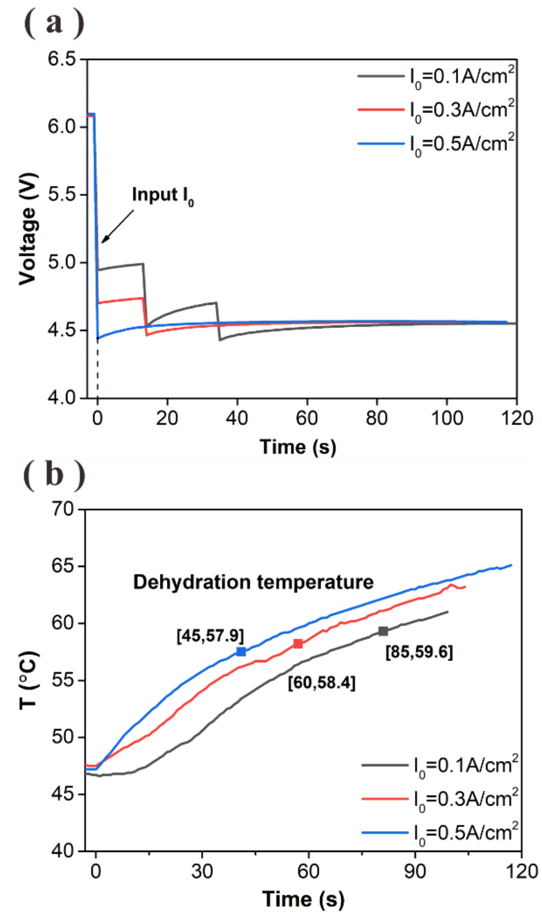

Fig.6. Voltage variations with time (a) and temperature variations with time (b). for step=15s and fixed gas flow rates. Influence of I_0

Fig.6b shows the corresponding curve of stack temperature over time, the heat generation rate is different due to the different starting currents. Therefore, the slope of temperature rise is not the same at the initial time. When starting with a high current density, it corresponds to a higher temperature rise rate. In addition, the stack temperature T_p also differs when the target load voltage is basically reaching stability. The value of T_p decreases gradually with the increase of I_0, This is because when higher current densities are activated, more membrane water is consumed to conduct the ions. At the same time, the higher current density will cause a large amount of heat to be generated quickly in a short time, and this heat will cause evaporation of much liquid water. Therefore, the membrane is easier to dry than the membrane in which the fuel cell started at a low current density, so the membrane dehydration temperature T_p will be lower.

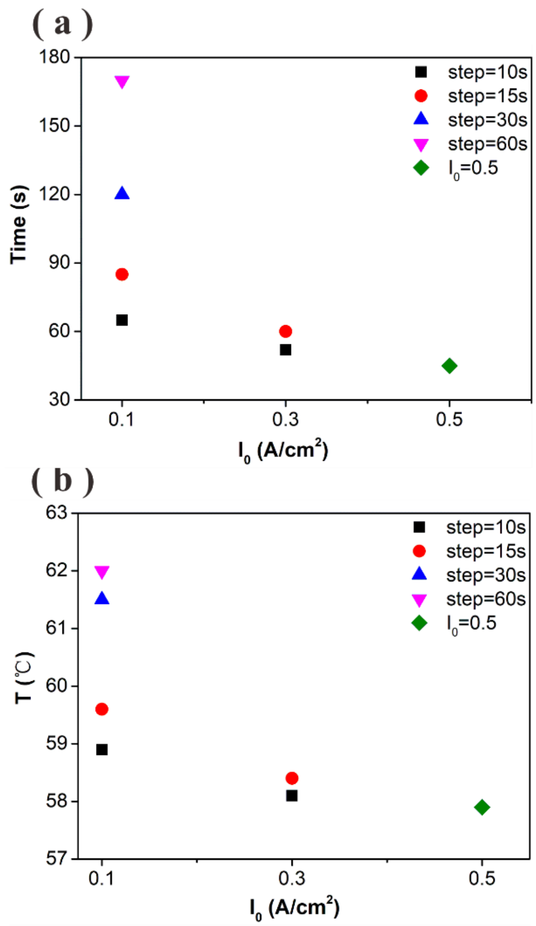

Fig.7. Variations for all conditions (a) start-up time. (b) The temperature of membrane dehydration. Influence of the ramp duration as a function of I_0.

In general, higher current density and shorter start-up steps shorten the start-up time. Comparing all start-up conditions of different current densities and step lengths together, it can be seen that from the 0.5A /cm^2 current density direct start-up corresponds to the shortest start-up time as shown in Fig.7a. The starting time of 0.3 A/cm^2, 5 s is almost the same as that of 0.1 A/cm^2 for 10s. Since the time steps of the 30s and 60s are too time-consuming in practical application, no more research will be done for the two modes.

However, from the point of view of stack temperature, a shorter start-up time obviously corresponds to a lower dry membrane temperature, The upper-temperature limit of the stack to be cooled during the start-up of 0.1 A/cm^2 current density is higher than that of other current densities. Considering that the heat is more difficult to be discharged in the underwater closed environment, it is necessary to sacrifice the start-up time appropriately in exchange for a higher operating temperature. Therefore, from Fig.7b, the low current density step start is more suitable for underwater vehicles

3.4 *Single cell performance*

This part studies the performance of single cell under different starting I_0. In order to more clearly show the performance of each cell under three current densities, we recorded the performance of the cell after a given load I_0 10s. As shown in Fig 4, the OCV difference of a single cell is very small. However, when the load is applied, the voltage gap between the cells gradually widens. As shown in Fig. 8, except for the No. 1 cell near the inlet, the performance of other single cells declines in the direction away from the inlet. This is mainly caused by the untimely gas supply of those cells away from the inlet at the moment of load supply. Therefore, when the current density is changed, the performance of the cell close to the gas inlet is relatively high, because the gas is easier to be transmitted to. It is worth noting that the voltage of No. 1 cell is not as high as we expected, but the performance of No. 2 cell is the best.

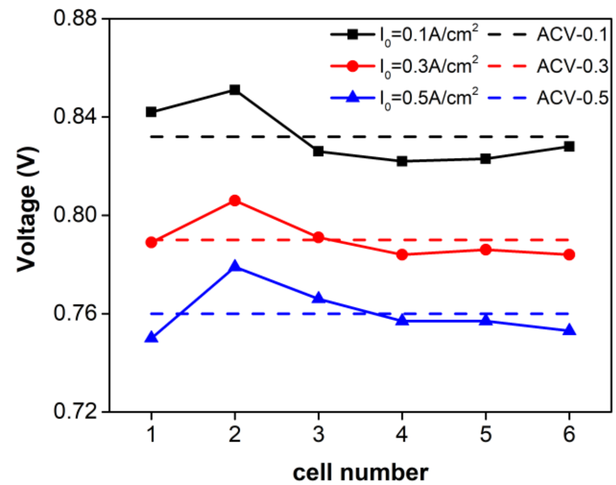

Fig.8. The voltage of 6 single cells and Average cell voltage（ACV）after 10s start-up under different I_0 in dead-end anode and cathode recirculation mode.

In many experiments, it is found that the main reason is that although the No. 1 cell is close to the gas inlet, the U-shaped stack design also makes it an exhaust outlet cell. Therefore, water will eventually gather at the No. 1 cell, affecting the reactant transmission in the No. 1 cell. Therefore, the performance is not as high as that of the No. 2 cell.

In addition, in the dead-end stack, it is found that with the increase of starting current density, the performance of No. 1 cell near the outlet gradually decreases, even below the average value.

To investigate whether the performance degradation is related to dead-end mode, we compared the performance of gas through. As shown in Fig 9, when gas passes through, the cells voltage basically follows the decreasing law from far away from the inlet to close to the inlet. The performance of No. 2 cell is the highest, similar to the law of dead-end mode. However, during the gas-through process, the performance of No. 1 cell did not decrease significantly with the increase of starting current I_0, and the voltage remained above the average value.

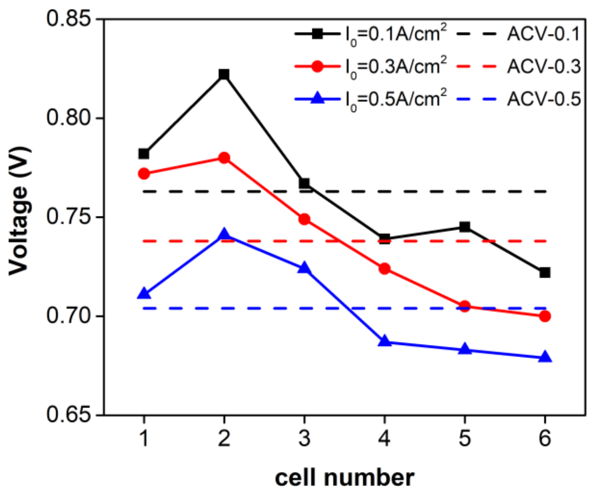

Fig.9. The voltage of 6 single cells and Average cell voltage （ACV） after 10s starting under different I_0 in gas-through mode.

This indicates that the dead-end structure has the problem that it is difficult to drain the accumulated water, and when starting at high current density, the instantaneous water production is more, so it is more likely to be submerged, resulting in a significant decline in performance.

4. CONCLUSION

The purpose of this study is to analyze the transient response of fuel cell stack during start-up and determine the corresponding operating parameters, so as to achieve rapid and stable dynamic response to power requirements. When the open circuit voltage OCV is reached for 10s, the current step is applied. The voltage change indicates that the response of the fuel cell depends on the initial current density I_0, the amplitude of the current density step and the gas supply mode.

in general:

1.When time step are fixed, the high current density start-up has faster response time. When starting current density are fixed, the shorter time step is used when the step current is loaded, and the shorter start time is also available.

2.At the same time, by comparing several start-up strategies, it is found that a shorter start-up step corresponds to a lower critical membrane dry temperature. Due to the fact that AUV uses more dry gas and takes into account the difficult of the heat dissipation in the enclosed space, AUV is more suitable for the start-up mode of low current density start-up and short step time.

3 In practical application, the dead-end stack has the problem of flooding at the outlet of the cell. When starting with high current density, the No. 1 cell is prone to flooding; Therefore, low current density is more suitable for the start-up of dead-end stack. At the same time, the problem of flooding of No. 1 cell can be reduced as much as possible by simplifying the pipeline at the outlet, avoiding upward arranged elbows and increasing the gas inlet pressure.

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