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Cold start characteristics of proton exchange membrane fuel cells under different purge conditions

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ABSTRACT

In this paper, a proton exchange membrane fuel cell (PEMFC) with reaction area of 25 cm^2 was purged with dry nitrogen before cold start at -10°C. The purge time was 10, 15 and 20 min respectively. The flow rate of purge gas was 1000, 1500 and 2000 mL / min respectively. And the assembling blots torque of the fuel cell was 1 and 4 N·m respectively. Through experiments to explore the influence of contact pressure, purge gas flow rate, and purge time on the PEMFC cold start performance. The results show that for dry gas purge, the running time at 1 N·m assembling bolts torque is longer than that at 4 N·m, because the former contact pressure is smaller than latter, indicating excessive contact pressure is not conducive to cold start. At the fixed purge gas flow rate, the running time is first increased and then decreased with increasing purge time, showing a maximum value at 15 min. At the fixed purge time, the running time is first increased and then decreased with increasing purge flow rate, showing a maximum value at 1500 mL/min.

Keywords: PEMFC, purge, cold start, contact pressure

1. INTRODUCTION

The difficulty of cold start of PEMFCs has become one of the main obstacles to their wide application as automotive power [1].

The PEMFC cold start refers to the process of starting from below 0°C and running to normal operating temperature (about 80°C). The main reason for the difficulty of PEMFC cold start is that water will be generated inside the PEMFC when it works. However, when the fuel cell temperature is below 0°C, the water inside the fuel cell will freeze, block the porous electrode and prevent the reaction gas from reaching the reaction site, resulting in the failure of PEMFC start-up. In addition, the residual water in the fuel cell will cause many adverse effects on it: as the volume of water increases after freezing, excessive residual water will damage the membrane electrode. Besides, the repeated freezing and melting of water on the surface of membrane will make the catalyst layer (CL) and gas diffusion layer (GDL) no longer fit closely, and even make the membrane crack, resulting in the intersection of reaction gases and reducing the life of PEMFCs [2,3]. Therefore, purge the PEMFC after it is shutdown can reduce the initial water content of PEMFC during cold start and reduce the icing probability, which is a necessary step to improve the cold start performance of fuel cell [4].

The purge process directly affects the water content in PEMFCs, and then seriously affects the cold start performance of PEMFCs. Therefore, to solve the problem of cold start by purge, it is necessary to understand the effect of purge conditions on the cold start performance of PEMFCs.

Regarding whether it is necessary to purge the cathode and anode sides at the same time, Sinha et al. [5] described the water removal process of PEMFCs during gas purge through numerical study. It was found that due to the reverse diffusion of water, a large amount of water will diffuse back to the anode, so the water removal effect of only purge the cathode is not obvious.

In terms of experimental research on how to improve the purge effect, Lee et al. [6] purged the cathode and anode at the same time with dry nitrogen gas when the temperature of the fuel cell was 10, 35, 65, and 90 °C, and compared the residual water in the fuel cell after purge at different temperatures. It was found that the residual water after purge at 65 °C and 90 °C is significantly reduced, and it is considered that high-temperature purge is more effective in removing water than low-temperature purge. Kim et al. [7] through experimental research found that adding a small amount of hydrogen to the cathode purge gas during purge is very effective to remove the water in the cathode, especially the residual water near the CL, and the damage of the CL is small after cold start.

In the modeling of analyzing the effect of purge temperature, flow rate, and humidity on the purge effect, Mu et al. [8] found that the overall dryness of fuel cells increases with the increase of gas flow rate, and the drying time required decreases with the decrease of relative humidity of purge gas. Pan et al. [9] and Sinha et al. [10] respectively studied the influence of purge conditions on the purge effect, and found that low relative humidity of purge gas, high purge gas flow rate and high purge temperature are conducive to improving the purge efficiency.

Based on the above research, it can be found that in the research on the effect of purge conditions on the PEMFC cold start, existing studies have focused on the temperature and flow rate of purge gas, purge time, the introduction of catalytic reaction during purge, etc., while there are few reports on the effect of purge under different contact pressures. Therefore, in this paper, the effects of contact pressure and purge conditions on cold start performance are studied.

2. EXPERIMENTAL SYSTEM AND METHODS

2.1 Fuel cell

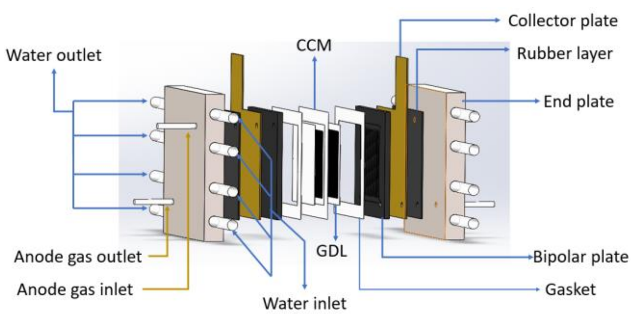

Fig. 1 Schematic diagram of fuel cell structure

Fig. 1 shows the fuel cell structure used in the experiment. In order to simulate the shutdown process before cold start, constant temperature water sources from the thermostatic water tank were introduced into the end plates on the cathode and anode sides respectively. In order to improve the uniformity of temperature, there were four inlet holes and four outlet holes in the end plates respectively. The specific fuel cell parameters are shown in Table 1.

Table 1 Basic parameters of fuel cell

Items	Parameters	Units
PEM type	Nafion212	
PEM thickness	50	μm
Reaction area	25	cm^2
Cathode / Anode platinum loading	0.6 / 0.4	mg/cm^2
Channel type	parallel	
Channel size (length × width × depth)	50×0.5×0.3	mm

2.2 Experiment system and conditions

Fig. 2 shows the system diagram of the PEMFC purge and cold start experiment. The temperature, humidity and flow rate of gas were controlled by the test system. The voltage change during cold start was also monitored in real time by the test system. The cryogenic chamber was used to cool the fuel cell. In the cold start experiment, in order to ensure the temperature of reaction gas was consistent with the temperature of the fuel cell, so as to avoid affecting the test results, after the reaction gas entered the cryogenic chamber, it must first passed through a long enough cooling coil to make the temperature of gas reach the temperature of cryogenic chamber before entering the fuel cell. The fuel cell temperature was measured by a K-type thermocouple with an accuracy of 0.1°C and was displayed in real time through a data collector. And the high frequency resistance of the fuel cell during purge process and cold start process was measured by the electrochemical workstation (INTERFACE5000E).

The whole experiment was carried out in the following four steps: The first step was steady-state operation stage. This step is to ensure that the initial state of the fuel cell at the beginning of each purge experiment was consistent. The second step was the purge stage. The third stage was to put the fuel cell into the cryogenic chamber and cool it down to the required temperature. The fourth step was the cold start stage.

After the fuel cell state was stable, applied the load to start the cold start test, and record the voltage and resistance changes of the fuel cell during the cold start. Table 2 shows the main experimental conditions in steady-state operation, purge, cooling and cold start.

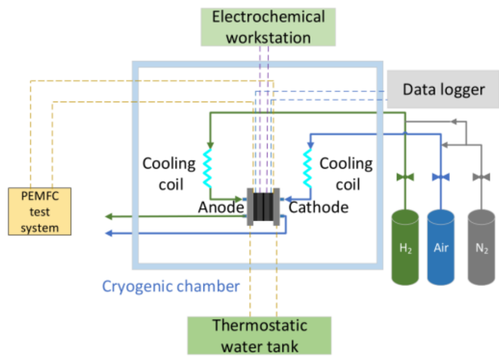

Fig. 2 Schematic diagram of PEMFC purge and cold start experimental system

Table 2 Experimental conditions

	Items	Parameters
Steady-state operation	Cell temperature	70°C
	Hydrogen flow rate	200 mL/min
	Hydrogen relative humidity	100%
	Air flow rate	600 mL/min
	Air relative humidity	70%
	Current density	0.04 A/cm^2
	operation time	30 min
Purge	Cell temperature	70°C
	Nitrogen flow rate	1000/1500 /2000 mL/min
	Purge time	10/15/20 min
Cooling	Cooling temperature	-10°C
	Cooling time	3 h
Cold start	Cell temperature	-10°C
	Hydrogen flow rate	95 mL/min
	Hydrogen relative humidity	0
	Air flow rate	226 mL/min
	Air relative humidity	0
	Current density	0.04 A/cm^2

2.3 Contact pressure measurement

The water content and liquid water distribution in the PEMFC affect the cold start performance. However, the contact pressure of PEMFCs has an impact on the liquid water movement and distribution, which affects the purge effect and the subsequent cold start performance. Therefore, it is necessary to study the cold start performance under different contact pressure. In this paper, the contact pressure distribution between cathode CL and microporous layer (MPL) under different assembling bolts torque was measured by placing pressure-sensitive paper between cathode CL and MPL. It can be seen from Fig. 3 that when the assembling bolts torque is 1 N·m and 4 N·m, the contact pressure under the rib is 0.5-0.75 MPa and greater than 2.50 MPa respectively, while that under the channel is 0.50 MPa and 1.25-1.50 MPa respectively.

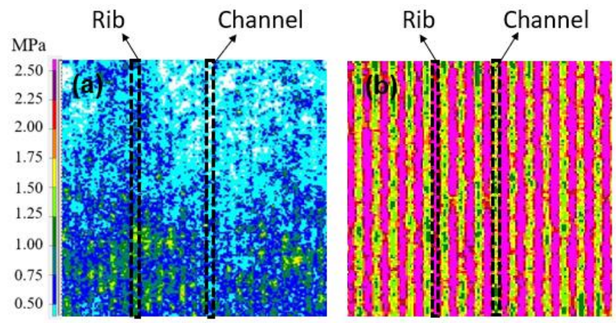

Fig. 3 Pressure distribution between CL and MPL: (a) 1 N·m and (b) 4 N·m

3. RESULTS AND DISCUSSION

3.1 Effect of contact pressure

Fig. 4 shows the changes of ohmic reactance and voltage with time during cold start at -10°C when the assembling bolts torque is 1 N·m and 4 N·m.

It can be seen from Fig. 4 that after purge under the same conditions, the running time with assembling bolts torque of 1 N·m is longer than that of 4 N·m, and the ohmic resistance with assembling bolts torque of 1 N·m is smaller than that of 4 N·m during cold start.

On the one hand, the contact pressure affects the initial state of cold start, on the other hand, it affects the cold start process. The initial state before cold start is mainly affected by purge after shutdown. Therefore, in order to fully understand the impact of contact pressure on cold start, this paper analyze it from two aspects: purge and cold start.

The liquid water in the gas purge is sequentially discharged from the flow channel, GDL, and membrane [5,9,10]. as shown in Fig. 5，In the first stage of purge, as the purge gas enters the channel, the ohmic resistance is almost the same under different contact pressures in the first 50s, which means that the water in the membrane has almost no change, that is, the water in the channel is removed during this period. Due to the large contact pressure when the assembling bolts torque is 4 N·m, the GDL is pressed into the flow channel deeply [11]. After the water in the channel is discharged, it will first take away part of the water vapor evaporated inside the GDL. Therefore, at the initial stage of purge, the ohmic resistance with assembling bolts torque of 4 N·m is slightly higher than that of 1 N·m, that is, the water removal rate is higher than 1 N·m. In the second and third stages of purge (after 200s as shown in Fig. 5), the porosity in the porous layer is reduced due to the large contact pressure, which makes the liquid water and water vapor flow difficultly in porous electrode [12]. Therefore, the water removal rate with assembling bolts torque of 1 N·m is significantly higher than that of 4 N·m at this moment.

It should be noted that from Fig. 4 (a) and Fig. 5, the initial ohmic resistance of the fuel cell before cold start is much less than that at the completion of purge (for example, the initial ohmic resistance before cold start is 0.019 Ohm and 5.3 Ohm at the completion of purge at 1 N·m). One of the reasons is that the ohmic resistance relaxation occurs after the purge is completed, so the ohmic resistance dropped significantly [13, 14]. Another reason is that after the fuel cell reached the set temperature, we observed that the ohmic resistance further dropped until it remained stable during the introduction of reaction gas. This phenomenon may be due to the internal water vapor in the fuel cell condense into liquid water during the cooling process. When the reaction gas enters the fuel cell, the liquid water is absorbed by the membrane.

At the beginning of cold start (as shown in Fig. 4), the ohmic resistance with assembling bolts torque of 4 N·m is higher than that of 1 N·m, which is opposite to the result at the end of purge. This is because there is redistribution of water in the fuel cell after stopping purge, so there is relatively more water not discharged with assembling bolt torque of 4 N · m, which may move to the CL or the interface between MPL and CL [15]. When the fuel cell temperature drops below 0°C, the water at the above position will freeze. When the assembling bolts torque is 4 N·m, the contact pressure between CL and MPL under rib or channel is large. The high contact pressure means that the porosity of GDL is significantly reduced, which makes it difficult for the reaction gas to diffuse to the reaction surface. Moreover, due to the reduction of porosity, the water generated by the reaction cannot be discharged in time, which is easy to form water accumulation and freezing [16]. For the above reasons, the assembling bolts torque of 4 N·m is easier to fail in cold start than 1 N·m.

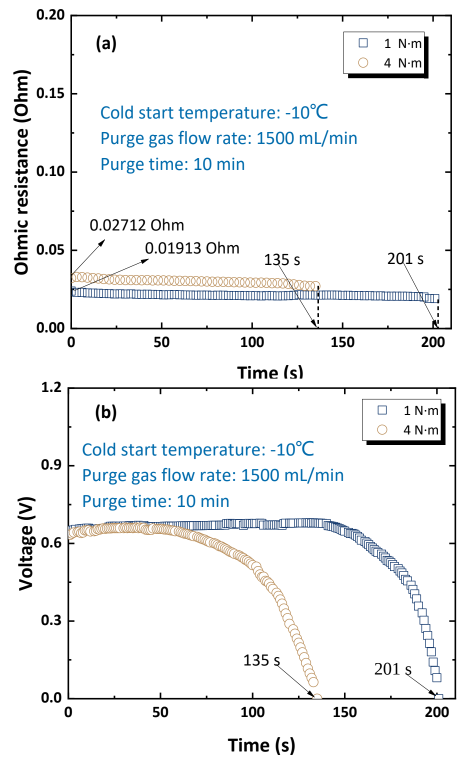

Fig. 4 Effect of assembling bolt torque on cold start: (a) ohmic resistance change and (b) voltage change

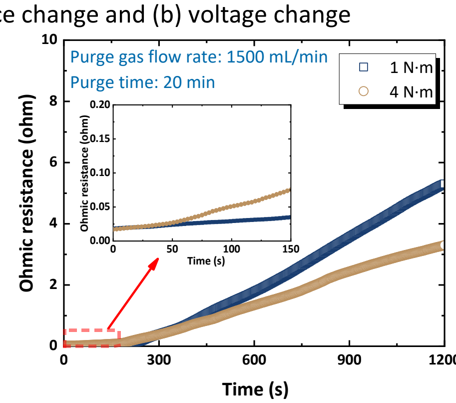

Fig. 5 Ohmic resistance change during purge process

3.2 *Effect of purge time*

Fig. 6 shows the changes of ohmic resistance and voltage with time during cold start at -10°C under different purge time. It can be seen from Fig. 6 that after purge at 1500 mL/min for 10, 15, and 20 min, the cold start process after purge for 15 min has the longest running time, while the cold start process after purge for 20 minutes has the shortest running time.

Because the flow rate of the purge gas is the same, the water removal rate is the same. When the purge time is short, there is more residual water in the fuel cell, so the absorption capacity of the membrane decreases, and the generated water is easy to freeze [17]. Due to the above reasons, the reaction gas cannot reach the reaction site of the CL, which accelerate failure of cold start. When the purge time is too long, the membrane will lose too much water. Although the produced water can be absorbed when the membrane is in a relatively dry state, which is beneficial to cold start [14]. However, excessive purge may cause damage to the membrane, affect the catalyst activity, and damage the ionomer in the CL which lead to a decrease in the active area [18]. The above reasons affect the cold start performance, this can also be proved from the highest ohmic resistance during cold start after purge for 20 min as shown in Fig. 6 (a). So, a too long purge time will also accelerate the failure of cold start. For cold start, it is not that the less residual water, the better.

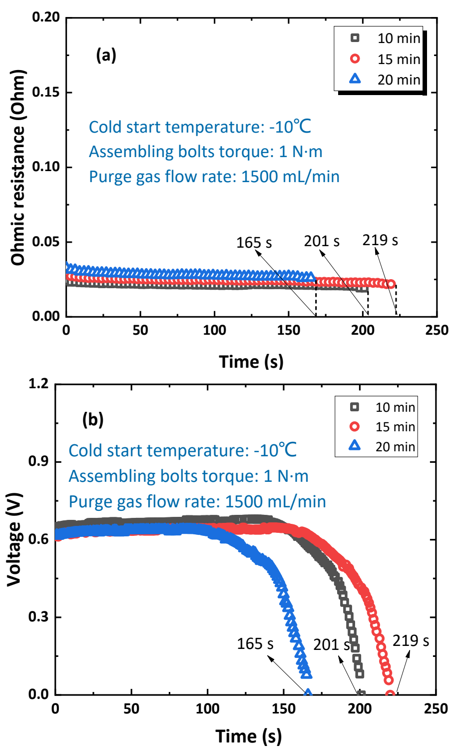

Fig. 6 The effect of purge time on cold start: (a) ohmic resistance change and (b) voltage change

3.3 *Effect of purge gas flow rate*

Fig. 7 shows the changes of ohmic resistance and voltage with time during cold start under different purge gas flow rate. It can be seen from Fig.7 that after purge with nitrogen at 1000, 1500 and 2000 mL/min for 10 min, the cold start process after purge at 1500 mL/min has the longest running time and lower ohmic resistance.

Because the greater the flow rate of purge gas, the greater the water removal rate, and the more residual water is removed in the same purge time [9]. The dry state of the membrane has greater water storage capacity, and the resistivity will increase which will increase the heat production of PEMFCs during operation. Despite the above advantages, when the fuel cell is in a relatively dry state, the ionomer in CL may shrink, change the reaction site and reduce the active area, which will affect the performance of cold start [18]. When the membrane is relatively wet, the membrane has poor water absorption capacity and cannot further absorb the produced water. Therefore, in the same purge time, too small or too large purge gas flow rate will accelerate the failure of cold start. For cold start, too much residual water is not conducive to cold start, but it is not that the less residual water the better.

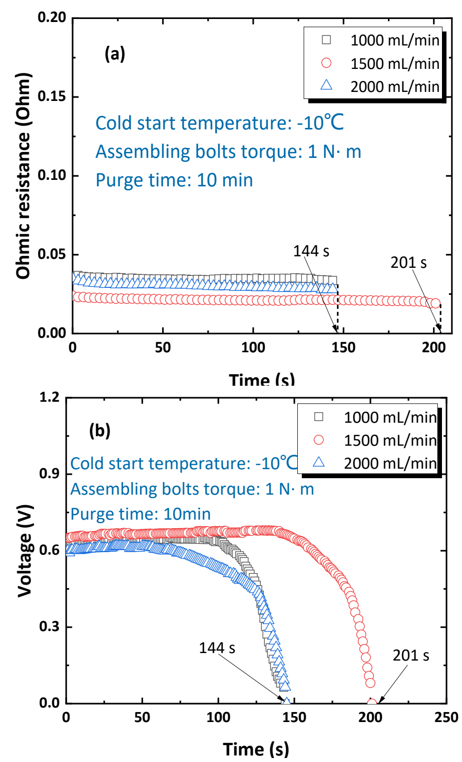

Fig. 7 The effect of purge gas flow on cold start: (a) ohmic resistance change and (b) voltage change

CONCLUSIONS

Purge before cold start can effectively discharge the residual water inside the fuel cell, which is conducive to the cold start and reduce the damage caused by icing. The contact pressure has an impact on the movement of liquid water inside the PEMFC, thus affecting the purge effect and the subsequent cold start process. Therefore, this paper carried out cold start experiments of PEMFCs under different contact pressure, different purge flow rate and different purge time, and explored the influence of various factors on cold start of PEMFCs.

1) The size of the assembling bolts torque reflects the size of the contact pressure. For PEMFC with assembling bolts torque of 1 N·m and 4 N·m, the cold start experiment indicates that the fuel cell with assembling bolts torque of 1 N·m shows better performance due to the change of pore size and the redistribution of water.
2) By changing the purge time and purge gas flow rate, it is found that purge before cold start (or after shutdown) is not the longer the time or the larger the flow rate, the better. After purge for 10, 15 and 20 min at the same flow rate, the PEMFC with purge time of 15 min has the best cold start performance; after purge at the flow rate of 1000, 1500, and 2000 mL/min for 10 min, the flow rate of 1500 mL/min has the best cold start performance.

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