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Effects of Freeze/Thaw Cycles and Gas Purging Method on Polymer Electrolyte Membrane Fuel Cells*

ZHANG Shengsheng(张生生)[a,b,*], **YU Hongmei**(俞红梅)[b], **ZHU Hong**(朱红)[a], **HOU Junbo**(侯俊波)[b], **YI Baolian**(衣宝廉)[b] **and MING Pingwen**(明平文)[b]
[a] School of Science, Beijing Jiaotong University, Beijing 100044, China
[b] Fuel Cell Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Abstract At subzero temperature, the startup capability and performance of polymer electrolyte membrane fuel cell (PEMFC) deteriorates markedly. The object of this work is to study the degradation mechanism of key components of PEMFC—membrane-electrode assembly (MEA) and seek feasible measures to avoid degradation. The effect of freeze/thaw cycles on the structure of MEA is investigated based on porosity and SEM measurement. The performance of a single cell was also tested before and after repetitious freeze/thaw cycles. The experimental results indicated that the performance of a PEMFC decreased along with the total operating time as well as the pore size distribution shifting and micro configuration changing. However, when the redundant water had been removed by gas purging, the performance of the PEMFC stack was almost resumed when it experienced again the same subzero temperature test. These results show that it is necessary to remove the water in PEMFCs to maintain stable performance under subzero temperature and gas purging is proved to be the effective operation.
Keywords polymer electrolyte membrane fuel cell (PEMFC), freeze/thaw cycle, electrode structure, performance degradation, gas purging

1 INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) is promising for its advantages of simple structure, relatively low operating temperature, high efficiency, convenient maintenance and rapid startup. PEMFCs can be used in many potential fields, especially as power sources for vehicles to replace normal combustion engine[1,2]. However, the availability of fuel cell vehicles is not quite close to us so far, although both concept design and demonstration have proved its feasibility. Actually, there are so many technical difficulties to be dealt with today, and the temperature impact is one of these issues encountered by the researchers and engineers.

In the winter time or at the cold polar region, ambient temperature may drop below zero. So it is highly necessary for vehicle fuel cells to keep the ability of rapid startup and good self-maintenance from low temperature to normal operating temperature when they are used outdoor, for example in the range of −40℃ to 80℃. Unfortunately, this demand is quite difficult for PEMFCs because of its high moisture content. Water is vital in PEMFCs to satisfy the hydration demand, which is the guarantee of favorable proton conductivity of the membrane and power generation capacity of PEMFCs. Water can be either brought into the fuel cell by external humidification or generated by electrochemical reactions[3]. When the fuel cell is shut down at the ambient temperature below freezing point, water will freeze into ice and the ice crystal will hold the reactant back from getting to catalyst surface. When the fuel cell comes to normal conditions gradually, the ice will melt into water again. Thus reduplicate phase transition of water in PEMFCs will cause nonreversible damage to the materials and even components of fuel cells. Cho *et al*.[4] figured out that the performance exhibited degradation after four thermal cycles when the temperature decreased to −10℃ and kept for 1h at this temperature. They also provided resistance difference between the electrode frozen and non-frozen through AC impedance measurement. Their conclusion was that the impedance between the electrode and membrane increased after freeze/thaw cycles while the impedance of the membrane kept unchanged. Research on this topic is underway and to date the publication about operation at subzero temperature is few. However, some patents could be found in this field. Most of the patents focused on alteration and optimization of fuel cell systems[5—8].

The objective of this paper is to study the subzero temperature effects on PEMFCs. Firstly, changes of electrode structure and fuel cell power generation capacity before and after freeze/thaw cycles were examined *via* different methods. As a method of water elimination, gas purging was also investigated during the freeze/thaw cycles.

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** To whom correspondence should be addressed. E-mail: shengshengzhang@163.com

2 EXPERIMENTAL

2.1 Test of the single fuel cell

A single cell ($1^{\#}$) was constructed with in-house membrane electrode assembly (MEA), two graphite bipolar plates and two organic glass end plates. The Nafion®212 membrane was sandwiched in two pieces of electrode and hot pressed for 1min (130℃ and 10MPa) to get the MEA. The Pt loading of the electrodes is 0.8 mg·cm^{-2} and the active area of the MEA was 2cm×2cm. Each side of the graphite bipolar plate has machined channels. Inside channels are reaction gases channels and the other side channels are provided for cycling water. The size of the whole cell is about 3cm×5cm×5cm. The fuel cell test station consisted of temperature controller, humidifier, mass-flow controller, pressure regulator and electrical load *etc*. The testing flow chart is the same as described in Ref.[1]. The single cell was fed with hydrogen as the fuel and oxygen as the oxidant. The molar stoichiometry ratio of the fuel and the oxidant was 1.5 and 2.5, respectively. Both hydrogen and oxygen were humidified through an external bubbler humidifier before they entered the cell. Cell temperature and humidifier temperature were both 50℃. Operating pressure was ambient pressure. The cell run at the above conditions and the polarization curves were tested before the cell was put into a climate chamber. Then, the chamber was cooled from 50℃ to −10℃ and kept the temperature at −10℃ for 1h for complete freeze. After that, the cell temperature was increased to 50℃ again to begin the next cycle. Fig.1 is the schematic of the whole freeze/thaw cycle.

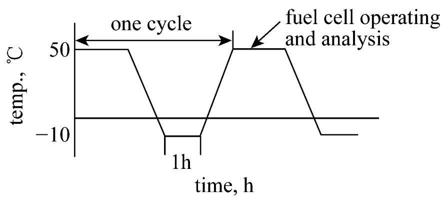


Figure 1 Schematic of the freeze/thaw cycles

Another single cell ($2^{\#}$) was constructed to test the gas purging effect at subzero temperature. The operating condition of the contrast cell was similar to the original cell except that the freezing/thaw process was companied with gas purging. Dry inactive gas was fed into the anode and cathode at the same time when temperature started to decrease. The pressure of the purging gas was kept in the range from 0.02 to 0.5MPa, and the gas flow rate was below 500ml·min^{-1}. The exact purging time depended on the relative humidity (RH) of the gas exiting from the cell.

2.2 Cyclic voltammetry

Cyclic voltammetry was applied on the single cell before and after 9 freeze/thaw cycles on Parstat 2273 advanced electrochemical system (Princeton, USA). Humidified nitrogen and hydrogen were fed into the cathode and the anode, respectively for 1h before the test. During the test, the temperature was hold at 50℃. The scan rate was 50mV·s^{-1}.

2.3 Test of the fuel cell stack

To investigate the purging effect on PEMFCs stacks at subzero temperature, a 6-cell PEMFC stack was constructed with the same MEAs as the single cell used. The effective area of each MEA is 128cm^2. The operating and polarization test condition of the stack was similar to the single cell except that the operating pressure was 0.1MPa (gage pressure). The specific procedure of gas purging was described in Ref.[9]. The main feature of the patent is that using some gases as purging medium to remove the redundant water remaining in the fuel cell after operation at subzero degree environment. The pressure and flux of the gas should be controlled during the purging procedure.

2.4 SEM measurement

Scanning electron micrography (SEM) was employed to study the effect of freezing and gas purging on the MEA structure. The specimens for SEM were prepared by cutting the cross section of the MEA by diamond knife at temperature of −100℃. The purpose of the measurement is to observe the micro texture of the MEA transect and estimate the alteration of membrane, catalyst layer and diffusion layers after freeze/thaw cycles. The SEM measurement was performed on Hitachi (Japan) S4300F scanning electronic microscope. Three MEA samples were original MEA, MEA of the single cell (after 9 cycles of freezing) and MEA of 6-cell stack (after 9 cycles of freezing and purging), respectively.

2.5 Mercury porosity analysis

The pore size distribution character of the MEAs was measured through mercury intrusion method with Poremaster GT60 (Quantachrome, USA). Also the samples are the same as used for SEM measurement. The pressure is from 1.38×10^3Pa to 4.13×10^7Pa (0.2 to 6. 0×10^4psi). The Hg contact angel is 140°. This technique is helpful to learn if the MEA structure changes after thermal cycles and if gas purging shows positive effect on protecting PEMFCs in subzero degree environment.

3 RESULTS AND DISCUSSION

3.1 Performance of single cell and 6-cell fuel cell stack

Figure 2 shows the comparison of the single cell polarization curves before and after 9 freeze/thaw cycles. Performance deterioration resulted from the thermal cycles can be easily observed. For example, the current density at 0.6V falls from 570mA·cm^{-2} to 420mA·cm^{-2}, almost decreased by 26%. When it comes to the second single cell with gas purging, the result is entirely different. From Fig.3, it can be found that the polarization curves of the contrast single cell was almost kept invariable during the 9 freeze/thaw and purging cycles. Fig.4 also suggested that the cell performance of the stack maintained nearly constant after 9 freezing and purging cycles. The open circuit voltage (OCV) of the single cell kept stable in the three experiments (about 0.96V each cell), which is consistent with the report of Cho *et al.*[4].The different results of the above experiments proved that gas purging can reduce the negative influence brought out by freeze/thaw cycles and improve the fuel cell durability at temperatures below 0℃.

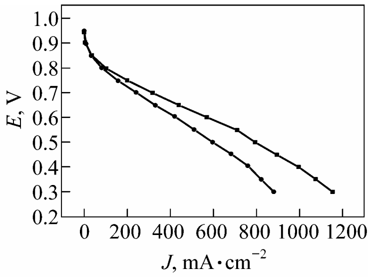


Figure 2 Effect of the freeze/thaw cycles from 50 to −10℃ on the polarization curves of the single fuel cell 1#
■ original; ● after 9 freeze/thaw cycles

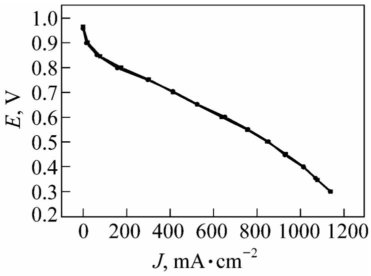


Figure 3 Effect of the thermal cycles from 50 to −10℃ with gas purging on the polarization curves of single cell 2#
■ original; ● after 9 purging and freeze/thaw cycles

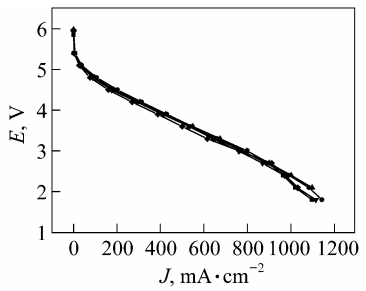
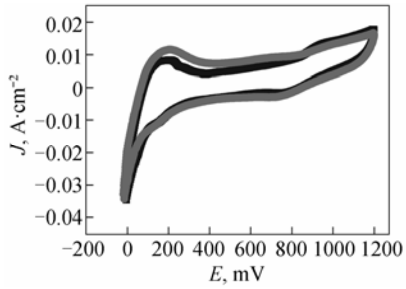


Figure 4 Effect of the thermal cycles from 50 to −10℃ with gas purging on the polarization curves of 6-cell PEMFC stack
■ 5; ● 6; ▲ 7; ▼ 8; ◆ 9

It is known that the density of water and ice at 0℃ are 0.9998 and 0.9168g·cm^{-3}, respectively. The volume of ice increases as much as 9%[10]. As a result, repeated freeze/thaw cycles certainly induces mechanical stress at water-rich region. The stress in turn causes the alteration in porous structure in the electrode. Possible negative results may include mean pore size increase, specific area decrease and electrochemical active area reduction. The structure change of the electrode will increase the ohmic resistance and charge transfer resistance of the fuel cell. Fig.5 shows the effect of the freeze/thaw cycles on cyclic voltammogram of the single cell. It could be found that the hydrogen desorption peak of the frozen cell was lower than that of the original cell, which indicated that the electrochemical activation of the catalyst was decreased after 9 freeze/thaw cycles. This degradation may be due to the agglomerate of Pt catalyst arisen by the micro-structure change during the repeated water freeze/thaw process.

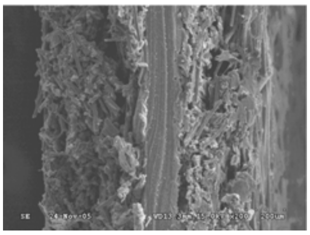


Figuer 5 Cyclic voltammogrames of the single cell before and after 9 freeze/thaw cycles
■ after 9 freeze/thaw cycles; ◆ original

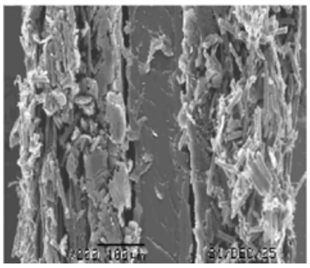
3.2 Structure of the electrodes

The purging procedure can remove most water in the fuel cell when it shuts down. So the performance degradation resulted from the water phase-transition can almost be avoided during freeze/thaw cycles. Physicochemical property measurement of the MEA confirmed the positive effect of gas purging on MEA structure during the course of reduplicate freeze/thaw cycles. Photos (a), (b) and (c) in Fig.6 are SEM photographs of the cross-section of MEAs freeze-free, after 9 freeze/thaw cycles, and after 9 freeze/thaw cycles with gas purging in turn. The micro structure of MEAs exhibited from SEM photographs suggests that the removing water can ultimately ensure the physical structure intact when undergoing the freeze/thaw procedure. There are no evident difference of the membrane, catalyst layer and diffusion layer between (a) and (c). In contrast, the distinctness between (a) and (b) is obvious, especially in some border area. Interfacial delamination between Nafion membrane and catalyst layer and breakage of diffusion layer can be found in Fig.6(b), which indicated that the repetitive freeze and thaw cycle damaged the MEA structure.

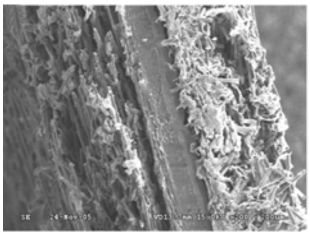
The porosity measurement result is in accordance with that of SEM analysis quite well. Fig.7 is the pore size distribution curves of the three MEA samples. 1, 2 and 3 here represent original MEA, MEA after 9 freeze/thaw with gas purging cycles and MEA after 9 freeze/thaw cycles, respectively. The pore size distribution of 1 and 2 coincide with each other approximately,



(a) Original MEA



(b) MEA after 9 freeze/thaw cycles



(c) MEA after 9 purging and freeze/thaw cycles

Figure 6 Scanning electron microscope pictures of the cross-section of MEAs

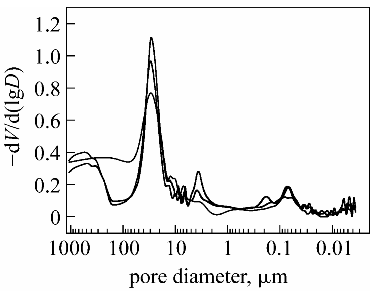


Figure 7 Pore size distribution of the original MEA and MEA after 9 purging and freeze/thaw cycles (measured by Mercury Porosimetry)

1—original MEA; 2—MEA after 9 purging and freeze/thaw cycles; 3—MEA after 9 freeze/thaw cycles

while the pore size distribution of MEA 3 is quite different from the other two samples as the SEM pictures showed. So, the results here also validated that the purging process could protect the structure of PEMFC component at subzero environment in some degree.

4 CONCLUSIONS

Water remaining in electrode of PEMFC is the immediate cause that results in structure change and performance degradation of PEMFCs in the thermal cycles from 50 to −10℃. Gas purging is an effective method in preventing sharp performance degradation during freeze/thaw cycles. The probably reason is that the structure breakage caused by phase transition of water can be avoided by effective water removing so that the components and performance of PEMFCs remain stable at subzero temperature conditions. Therefore, the method proposed in this paper is helpful to improve the durability of PEMFCs and its availability at subzero temperature.

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