Research on the Performance of Perfluorinated Proton Exchange Membrane Made by Flow Casting*

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Abstract: In this paper, the mechanical strength and electrochemical performance of perfluorinated proton exchange membrane made by flow casting were studied. Compared with Nafion membrane, those performances of the flow casting membrane were similar. They are different in the surface conformations.

Key words: perfluorinated ionomer membrane; fuel cell; flow casting
CLC number: TM911.48 **Document code**: A **Article ID**: 0529-6579(2003)S1-0050-03

1 Introduction

The perfluorinated proton exchange membrane is a commercially available perfluorosulphonate cation exchange membranes commonly used as a perm-selective separator in chlor-alkali electrolysis and as the electrolyte in solid polymer fuel cells[1-3]. This usage arises because of its high mechanical, thermal and chemical stability coupled with its high conductivity and ionic selectivity.

The perfluorinated proton exchange membrane can be made by the methods of extrusion[4] and flow casting. To the first method, the production process is very complex and the cost of equipment is high. Therefore up to now, the perfluorinated proton exchange membrane can be made only in some companies of US and Japan. The method of flow casting is entirely different from extrusion, it can not only simplify the production process, but also decrease the cost. Moreover, the flow casting membrane's performances are equal to the extrusion membrane (Nafion) in many fields.

By referring to the making methods of membrane in the relating fields[5,6], the flow casting membranes are made successfully. In this paper, the mechanical strength and electrochemical performance of perfluorinated proton exchange membrane made by flow casting were studied.

2 Experimental Part

2.1 Materials and apparatus

Nafion (5%), Nafion 112, Nafion 117, DuPont, Atomic Force Microscape, DI Co.
Fuel cells instrument (Model FYCY-5), Fuyuan Co. Ltd., Instron 118, English

2.2 The making method and measure of flow casting

2.2.1 The making process

Flow casting: the solution of Nafion is cast on moulding board, and then dried in high temperature air.

Pretreatment: treat the flow casting membrane in the solution of H_2O_2 and HNO_3 to wash away the impurity in membrane.

2.2.2 Mechanical strength

Put the membrane on the machine of Instron118 to test the mechanical strength, in the condition of 25 ℃ and humidity 50%.

2.2.3 Electrochemical performance

Use the pretreatment membrane to make the membrane-electrode assemblies (MEAs) and test its electrochemical performance in the FYCY-5, which is designed to measure the performance of fuel cells.

3 Results and discussions

In this part, the mechanical strength and electrochemical performance of extrusion membrane (Nafion) and flow casting membrane are compared to study the influence of different making methods on the perfluorinated proton exchange membrane.

3.1 The mechanical behavior of flow casting membrane

When used in the fuel cells, the perfluorinated proton exchange membrane should be flexible and have adequate mechanical strength. It can be seen from Tab. 1, the difference between flow casting membrane and

* Received 10 December 2002; Accepted 18 April 2003
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Nafion in mechanical performance isn't great. Thus the flow casting membrane can be used in fuel cells.

Tab.1 The mechanical behavior of flow casting membrane

No.	E_t/MPa	ε_t/%	σ_t/MPa
1	178	95	33
2	111	125	27
3	187	110	25
Nafion117	163	125	22

E_t: elastic modulus; ε_t: breaking extension; σ_t rupture intension; Test temperature 25 ℃, humidity 50%

3.2 The electrochemical performance of flow casting membrane

It is well known that the perfluorinated proton exchange membrane is the absolutely necessary part in fuel cells. Therefore besides, its electrochemical performance is more important than its mechanical behavior. The studies on it are followed.

(1) The comparison of flow casting membrane and Nafion in the electrochemical performance of fuel cell.

Fig.1 reveals that the current density of flow casting membrane and Nafion is equal when the cell voltage is from 800 to 1000 mV. But when cell voltage is in the range of 200 ~ 800 mV, it is obvious that the slope of curve of flow casting membrane is lower than that of Nafion in the voltage-current density curve. That is to say, the output power of flow casting membrane is higher and its electrochemical performance is better.

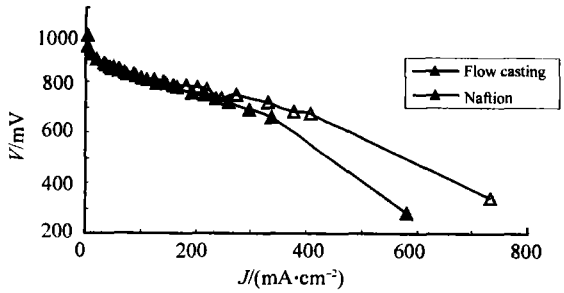

Fig.1 The comparison of flow casting membrane and Nafion in the performance of fuel cell $p(H_2)/p(air) = 0.1/0.1$, $T(cell) = 25$ ℃, electrode area = 5 cm²

(2) The influence of thickness of flow casting membrane on the performance of fuel cell.

According to the figures given in the Fig. 2, the thickness of flow casting membrane is tightly connected to the performance of fuel cell. With the increase of thickness, the slope of voltage-current density curve is increased and the performance of fuel cell declined. The chief reason is that the thickness has obvious influence on the internal resistance. The thicker membrane is, the higher internal resistance is. Therefore in the same condition, the thin membrane has more advantage in conductance radio. But if the membrane is too thin, the hydrogen gas is likely to leak out and then result in the decline of cell voltage, even the destruction of fuel cells.

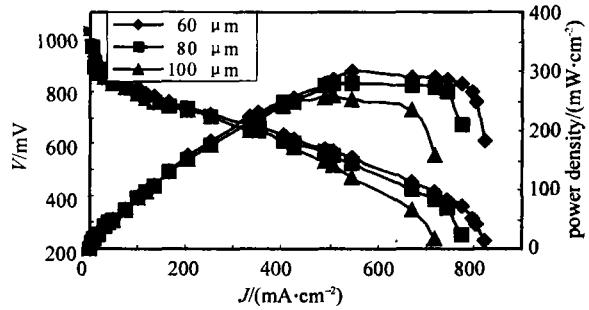

Fig.2 The influence of thickness of flow casting membrane on the performance of fuel cell $p(H_2)/p(air) = 0.1/0.1$, $T(cell) = 25$ ℃, electrode area = 5 cm²

3.3 The infrared spectra of flow casting membrane

As reported in many articles, the perfluorinated proton exchange membrane leads to degradation reaction in its produce process. Is there degradation reaction in the process of flow casting? To answer this question, we research the flow casting membrane by infrared spectrum and compare its infrared spectra with Nafion's.

According to the figures given in the Fig.3 and Fig. 4, the infrared spectras of flow casting membrane and Nafion are similar, not only in their characteristic spectrum's peak position but also in peak height and peak width. That is to say, the component of flow casting membrane is the same to that of Nafion and there is not degradation reaction.

3.4 The atomic force microscope photo of flow casting membrane

The surface morphology of perfluorinated proton exchange membrane has some influence on the electrochemical performance of perfluorinated proton exchange membrane. In the paper, atomic force microscope (AFM) is used to study the relationship of making method with the membrane's surface morphology.

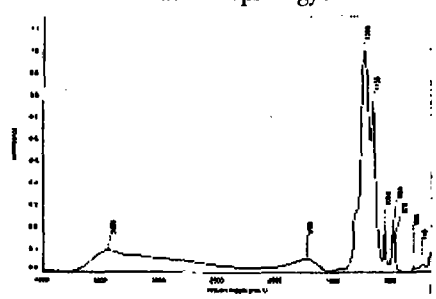

Fig.3 The infrared spectra of flow casting membrane

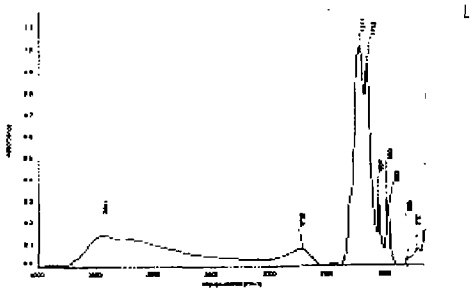

Fig.4 The infrared spectra of Nafion

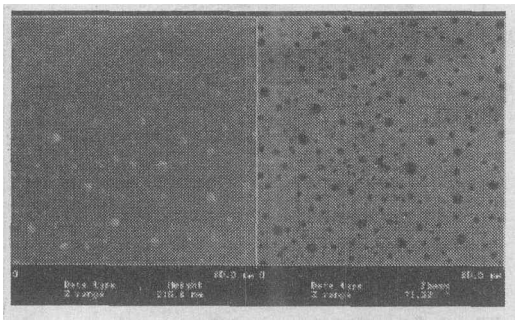

Fig.5 The AFM photo of flow casting membrane

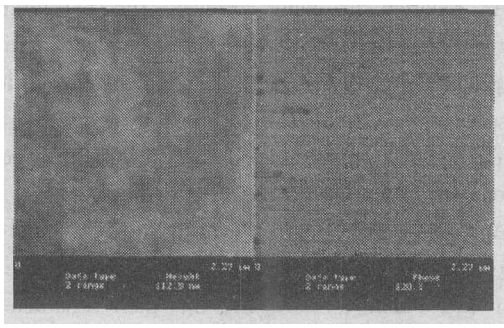

Fig.6 The AFM photo of Nafion

From the tables we can also see that there is obvious distinction in the surface morphology between flow casting membrane and Nafion. The distinction in making methods is the mainly reason which results in such variety of surface morphology. The Nafion (extrusion membrane) is made from melted resin. As regards the flow casting membrane, the making process of it is completely different from that of the extrusion membrane. Because the flow casting membrane is made from the solution of Nafion, there is obvious volatilization of solvent in the process of flow casting and drying which lead to the unevenness on its surface. As to the uniformity and unevenness on these two kinds of membranes' surfaces whether there is great influence on the electrochemical performance of fuel cells made from them will be researched further.

4 Conclusion

According to those above-mentioned discussion, we can safely draw this following conclusions:

(1) The difference between flow casting membrane and extrusion membrane (Nafion) in mechanical performance and electrochemical performance isn't great. Thus the flow casting membrane can be used in fuel cells.

(2) With the increase of flow casting membrane's thickness, the slope of voltage-current density curve increased and the performance of fuel cell declined.

(3) There is not degradation reaction occurred in the production process of flow casting membrane.

(4) There is obvious difference in the surface morphology between flow casting membrane and extrusion membrane (Nafion) because of the difference of making methods.

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流延法制全氟磺酸质子交换膜的性能研究

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摘 要:全氟磺酸质子交换膜作为一种固体聚合物电解质,它具有化学稳定性和热稳定性好、电压降低、电导率高、机械强度高等优点,可在强酸、强碱、强氧化剂介质和高温等条件下使用,并已成为氯碱工业及燃料电池生产中最关键的组件。对流延法制全氟磺酸质子交换膜的物理机械性能和电性能进行了研究,并与挤出法制全氟磺酸质子交换膜比较,认为流延法膜和挤出法膜物理机械性能和电性能相差不大,但在表面形态上具有较大差异。

关键词:全氟磺酸质子交换膜;燃料电池;流延法

中图分类号:TM911.48 **文献标识码**:A