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Electrospun Poly(Ether Sulfone) Membranes Impregnated with Nafion for High-Temperature Polymer Electrolyte Membrane Fuel Cells

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Abstract : Electrospun poly(ether sulfone) (PES) membrane impregnated with Nafion (PES-N) have been developed for high-temperature polymer-electrolyte membrane fuel cell (HT-PEMFC). The PES-N obtains highly thermal stability up to 430°C, which is higher than that of the commercial Nafion 212. The PES-N membrane shows a good proton conductivity of about 10^{-2} S cm^{-1} in a temperature range from 75°C to 120°C. The membrane-electrode assembly (MEA) with the PES-N membrane exhibits a current density of 1.697 A cm^{-2} at 75°C, and 0.813 A cm^{-2} at 110°C when the applied voltage is 0.6 V, whereas the MEA with the Nafion 212 membrane shows the current density of 0.647 Acm^{-2} at 110°C. The results suggest that the PES-N can be a good candidate for a polymer electrolyte membrane of the HT-PEMFC.

Keywords : Polymer Electrolyte Membrane; Nafion; Poly(ether sulfone); Electrospinning; Thermal Stability

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) have been considered as an environment-benign technology due to their pollution-free operation, high energy conversion efficiency, and low maintenance costs for transportation and stationary application.[1-2] However, commercialization of the PEMFC has been limited by several technical problems; high cost, low proton conductivity at low relative humidity, high fuel crossover, and poor mechanical properties at high temperatures above 100°C.[3] Over the last decades, numerous researches have been reported to overcome these problems.[4-6] For the high-temperature PEMFC (HT-PEMFC), it is very important factor to develop the membrane with high proton conductivity and chemical and thermal stability at high temperatures above 100°C. A perfluorosulfonic acid (Nafion) has been widely used as a polymer electrolyte membrane of the PEMFC because of its high proton conductivity.[7] Nevertheless, the application of these polymers has been limited due to high cost of their productions and low chemical and thermal stability at the temperatures higher than 80°C.

Poly(ether sulfone) (PES) has been suggested as a polymer electrolyte membrane of the HT-PEMFC. The PES is a high-performance engineering thermoplastic which consists of repeated phenyl and sulfone groups.[8] It shows a good chemical, mechanical and hydrolysis stability at the temperature above 100°C, and therefore it can be used for the HT-PEMFC. The diaryl sulfone groups in the polymer chains are mainly responsible for these characteristics, which provide chain flexibility as well as aromatic structures. Despite the desirable characteristics for the HT-PEMFC, the untreated PES membrane exhibits extremely low proton conductivity.

Electrospinning of polymer solutions is an efficient method of preparing microporous membranes. The electrospinning method has been widely used in various fields such as lithium secondary batter-

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ies, biomedical materials, filters and fabrics.[9-10] In particular, the well-connected fibrous structures formed by electrospinning would offer better mechanical and chemical properties to the membrane in the PEMFC. However, it has been rarely applied to fabricate the polymer electrolyte membrane of the PEMFC.[11]

In this study, we prepared Nafion-impregnated electrospun PES membrane (PES-N) not only to overcome the low chemical and thermal stability of the Nafion at high temperatures[12] by introducing the well-connected PES fibrous structures but also to provide high proton conductivity to the fibrous PES backbone by impregnating Nafion. The electrochemical properties of the PES-N membranes and membrane-electrode assemblies (MEAs) were investigated at different temperatures.

2. Experimental Section

Microporous PES membranes with a thickness of about 200 μm were prepared by using an electrospinning method.[13,14] The poly(ether sulfone) (PES 6020P, Victrex) was dissolved in a mixed solvent (acetone / dimethylacetamide = 5/5, w/w) to prepare the PES solution with a concentration of 25 wt.%. The PES solution was stirred at 80°C for 4 h. The electrospinning (DASAROBOT, DTR2-3310-S-SG model) was conducted at a voltage of 13 kV with a flow rate of 50 μL min^{-1}. The temperature and humidity were remained to 25°C and 30%, respectively. The distance between the nozzle and collector was 16 cm. The electrospun PES membranes were dried by vacuum-drying at 80°C for 24hr to remove the residual solvent. The Nafion solution (5 wt.% solution in lower aliphatic alcohol/H_2O mix, Sigma-Aldrich) was impregnated to the electrospun PES membranes. The total amount of the Nafion solution impregnated was 8 g. The Nafion-impregnated PES membrane (PES-N) were dried at 80°C to evaporate the solvent, and finally dried in a vacuum oven at 100°C for 24hr.

The morphological characteristics of the membranes were investigated by using a scanning electron microscopy (SEM, S-4300, Hitachi) after sputtering gold on the surfaces of the samples. The gas permeation test was conducted by using H_2 gas in a pressure range of 0.5~3 $kg_f cm^{-2}$. The flux of H_2 gas was measured by a bubble flow meter.[15] The thermal stability of the membranes was measured by thermo-gravimetric analyzer (TGA, Pyris Diamond, PerkinElmer) under N_2 atmosphere with a heating rate of 10°C min^{-1} in the range of 30~800°C. The proton conductivity of the membranes was measured by AC impedance spectroscopy (PGSTAT-30, Autolab impedance analyzer) in the frequency range of 0.1~10,000 Hz at an amplitude of 10 mV after stabilizing the membranes at different temperatures and relative humidity (RH). The catalyst slurry was prepared by mixing 40 wt.% Pt on carbon black (Johnson Matthey), isopropyl alcohol and 5 wt% Nafion (EW 1100) solution. It was sonicated for 3 min and stirred for 5 min, which was repeated 5 times. Membrane-electrode assembly (MEA) was prepared by spraying the catalysts on both sides of the membrane. The active electrode area for a single cell test was 4 cm^2 with platinum loading of 0.4 mg cm^{-2} for anode and cathode. The sing cell test was set up with the MEA, gas diffusion media (SGL 10BC), Teflon gaskets and graphite blocks. The fuel (H_2, 200 mL min^{-1}) and oxidant (O_2, 300 mL min^{-1}) gases were passed through humidifiers before feeding the gases into the cells. The cell performances (I-V curves) were measured by using an electric load (KFM2030, Kikusui).

3. Results and Discussion

3.1 Morphological characteristics

The morphologies of the electrospun PES and the PES-N membranes were detected by using SEM, and the corresponding images are shown in Fig. 1. The fibrous PES membrane showed a microporous structure with the well-connected fibers in a diameter of 0.8~2 μm (Fig. 1a). After impregnating Nafion to the fibrous PES, the smooth and densified surfaces were observed in the PES-N membrane. The electrospun PES fibers existed inside the membrane, remaining their fibrous structures (Fig. 1b), which would reinforce the mechanical strength of the membrane.

3.2 Hydrogen permeability and thermal stability

In the PEMFC operation, it is important to prevent gas cross-over through the membranes because

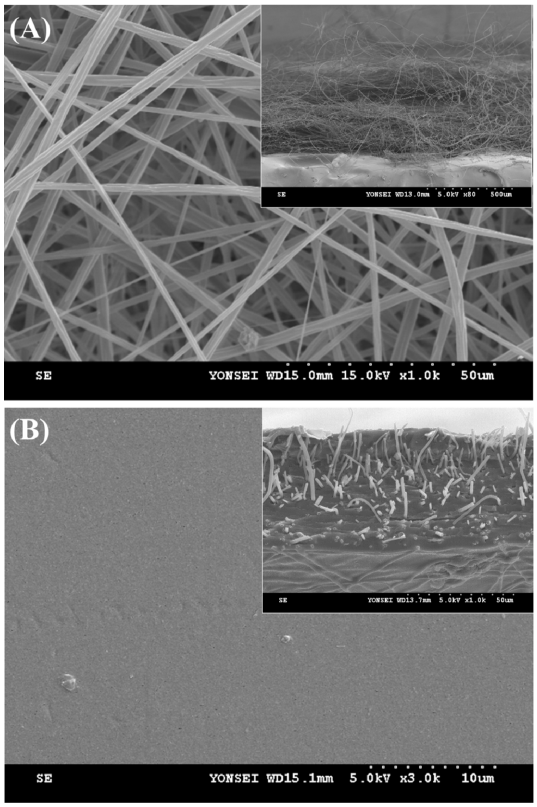

Fig. 1. SEM images of (a) electrospun PES and (b) PES-N (the insets represent the cross-sectional SEM images).

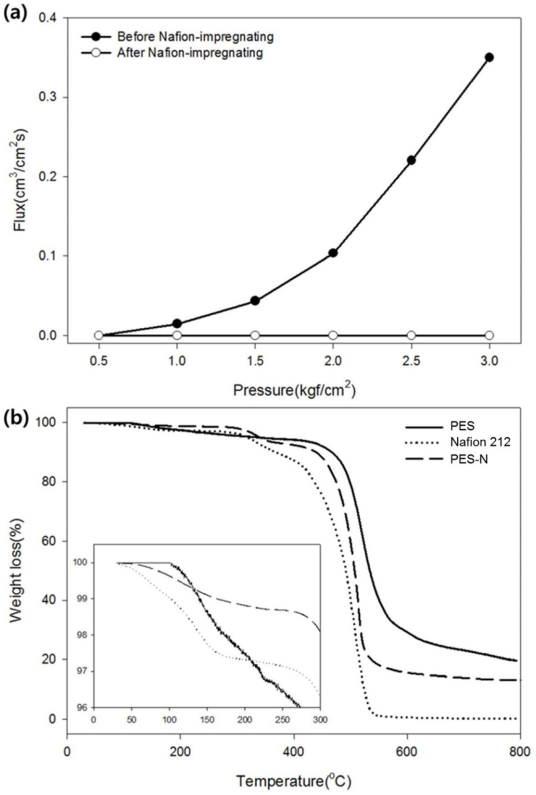

Fig. 2. (a) H_2 permeability of the PES and PES-N membranes and (b) TGA curves of the PES, Nafion 212 and PES-N.

open circuit voltage (OCV) and durability of the PEMFCs can be improved. Thus, H_2 permeation test was conducted, and the flux results are presented in Fig. 2a. The H_2 gas flux through the electrospun PES was $1.47 \cdot 10^{-2}$ cm^3 cm^{-2} s at a pressure of 1.0 kg_f cm^{-2}. As the pressure increased, the H_2 gas flux through the electrospun PES was sharply increased with a parabolic shape. By contrast, the gas flux through the PES-N membrane was remained to almost zero despite increase in the pressure, which demonstrates that the PES-N membranes are dense enough to prevent gas cross-over.

The TGA was measured to evaluate the thermal stability of the PES, Nafion 212, and PES-N, and the corresponding results are shown in Fig. 2b. The temperatures where the weight loss firstly appeared were about 50, 70, and 110°C in the Nafion 212, PES-N, and PES, respectively. The weight loss up to 150°C may be attributed to H_2O evaporation. From 250°C, the weight loss may be due to desulfonation. It suggests that although the degradation of the polyaromatic backbone started above 400°C, the cell performance may start to be degraded below that temperature due to the desulfonation that lowers proton conductivity of the membranes. At this point, the PES-N membrane showed the lowest weight loss from 150°C to 250°C where the desulfonation mainly occurs, which means that the PES-N membrane can be suitable for the polymer electrolyte membrane of the HT-PEMFC.

3.3 Electrochemical characteristics

Fig. 3 shows the I-V curves of the PEMFCs with the PES-N and Nafion 212 membranes at different temperatures. The PEMFC with the PES-N membrane had the current density of 1.69 A cm^{-2} at 75°C when the applied voltage was 0.6 V. The cell performance was slightly decreased with increase in the temperature to 90°C, showing the current den-

sity of 1.45 A cm^{-2} at the same applied voltage. However, as the temperature increased into 110°C and 120°C, the cell performances were greatly degraded. This may be due to change of the relative humidity. The proton conductivity of the Nafion largely depends on the humidity, and therefore, the degradation of the cell performances would be attributed to the low humidity under the elevated temperature. The open circuit voltages of the cells were around 0.98 V at all temperature ranges, which indicates that the PES-N membranes successfully prevented gas cross-over even at the high temperatures. In comparison of the cell performances between the PEMFCs with the PES-N and Nafion 212 membranes, the cell performances of both cells were similar at 75°C (Fig. 3b). However, the PEMFCs with the PES-N membrane had higher performance than the PEMFC with the Nafion 212 at 110°C, showing the current density of 0.813 Acm^{-2} and 0.647 Acm^{-2} at 0.6 V, respectively. The higher performance of the PEMFC with the PES-N membrane may be due to less desulfonation of the PES-N membrane at high temperatures as shown in Fig. 2b.

To evaluate the electrochemical characteristics, the electrochemical impedance spectroscopy (EIS) was measured on the PEMFCs with the PES-N membranes at different temperatures. The intercept between the impedance semi-circle at high frequency and the real axis refers to the ohmic resistance. A diameter of the impedance semi-circle indicates the polarization resistances (the sum of the electrode resistances and interfacial resistances between the electrodes and membrane).[16] The ohmic resistances were 0.032 and 0.036 at 75°C and 90°C, respectively (Fig. 4a). However, the ohmic resistances were increased to 0.072 and 0.125 as the operating temperatures rose to 110°C and 120°C, respectively. It corresponds to the results of the I-V curves. The polarization resistances showed

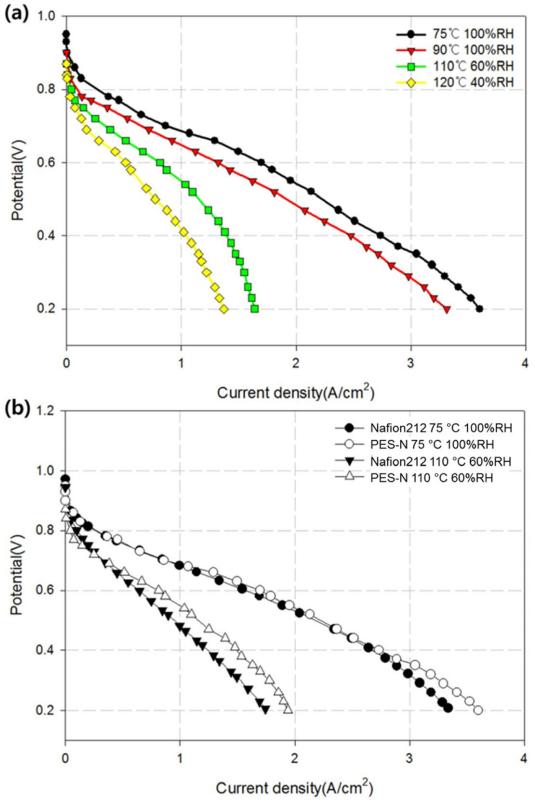

Fig. 3. I-V curves of the PEMFC (a) with the PES-N membrane and (b) with the PES-N and Nafion 212 membranes at different temperatures.

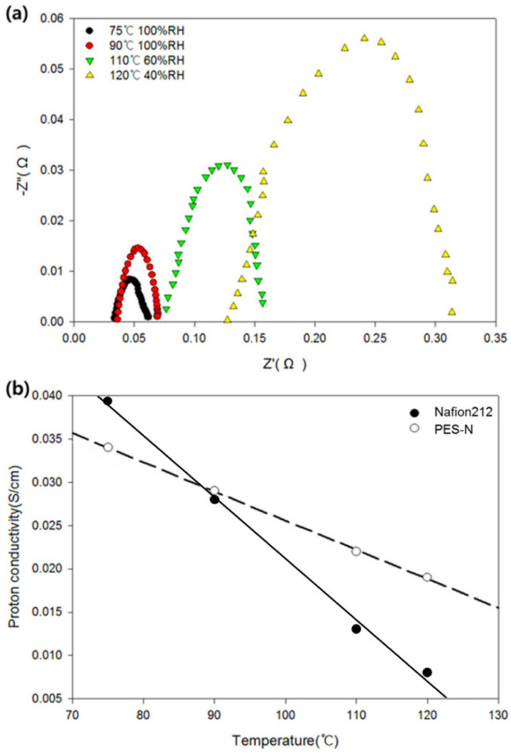

Fig. 4. (a) Electrochemical impedance spectra of the PEMFCs with the PES-N membrane at different temperatures and (b) comparison of the proton conductivities between the PES-N and Nafion 212 membranes.

similar tendency with the ohmic resistances, changing from 0.05 at 75°C to 0.38 at 120°C. For the proton conductivity, the PES-N membrane was changed in the conductivity from about $3.6\cdot10^{-2}$ S cm^{-1} at 75°C to $1.9\cdot10^{-2}$ S cm^{-1} at 120°C, whereas the Nafion 212 membrane was significantly decreased from $3.8\cdot10^{-2}$ S cm^{-1} at 75°C to $8.0\cdot10^{-3}$ S cm^{-1} at 120°C (Fig. 4b). It demonstrates that the PES-N membrane suppresses the desulfonation with increase in the temperatures. In other words, the PES-N membrane can be more suitable than the pure Nafion for the polymer electrolyte membrane of the HT-PEMFC.

4. Conclusions

The electrospun PES membrane impregnated with Nafion was prepared for a polymer electrolyte membrane of the PEMFC. The PES-N membrane showed high thermal stability up to about 430°C, which is superior to the commercial Nafion 212. Furthermore, the desulfonation can be suppressed in the PES-N membrane at high temperatures, which ensures the desirable proton conductivity at the temperature regime. The PES-N membrane showed a proton conductivity of $1.9\cdot10^{-2}$ S cm^{-1} at 120°C, whereas the Nafion membrane had $8.0\cdot10^{-3}$ S cm^{-1} at 120°C. The current densities of the PEMFC with the PES-N membrane were about 1.697 Acm^{-2} at 75°C and of 0.813 Acm^{-2} at 110°C when the applied voltage was 0.6 V, which is better than the PEMFC with the Nafion membrane. As a result, the electrospun PES-N can be a suitable candidate for the polymer electrolyte membrane of the HT-PEMFCs.

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