Annealing Effect of Perfluorosulfonated Ionomer Membranes on Proton Conductivity and Methanol Permeability

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ABSTRACT: Perfluorosulfonated ionomer (PFSI) was synthesized and PFSI membranes were prepared via a solution-cast method and annealed at different temperatures from 150 to 230°C. The annealing effect on water content, proton conductivity, and methanol permeability were reported and discussed. X-ray diffraction and small angle X-ray scattering were used to test the structure of the membranes. It was found that annealing increased the proton conductivity of the membranes because heat-treatment helped to free the sulfonic groups that were buried in the polymer segments and form more organized ionic clusters. Water content and methanol permeability of the annealed membranes decreased with increasing annealing temperature. Simultaneously, annealing induced more compact chain packing structure, which eventually affected the transport of the proton and methanol through these ionomer membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 396–402, 2008

Key words: annealing; ionomers; membranes; methanol permeability; proton conductivity

INTRODUCTION

Because of high mechanical strength, excellent thermal stability, and good chemical stability, perfluorosulfonated ionomer (PFSI) membranes are becoming more and more attractive owing to their important applications in electrochemical processes.[1,2] Recently, direct methanol fuel cells (DMFCs) have demonstrated improved performance,[3,4] in which PFSI membranes are selected to be used to transfer protons. Compared to fuel cell systems using direct H_2, DMFCs have the advantage of simple system design and cell operation, and they may even achieve higher overall energy efficiency with further development.[5] But one of the major obstacles that currently prevent the widespread commercial applications of DMFCs is the crossover of methanol through the polymer electrolyte membrane.[6,7] Now it has been realized that methanol crossover to the cathode not only lowers fuel utilization efficiency but also adversely effects the oxygen cathode, resulting in poorer cell performance.[8]

After Moore and Martin developed a solution processing procedure that produces solution-cast PFSI membranes that have excellent mechanical properties,[9] it was found to be a good method to prepare PFSI chlor-alkali membranes,[10] coatings of modified electrodes,[11] PMFCs and DMFCs membranes,[12,13] and recast membranes.[14] In the past decades, research work on perfluorosulfonated membranes mainly focused on as received melt-extruded Nafion® membranes. However, only a few articles reported on the morphology of solution-cast PFSI membranes, especially few for the annealed ones. Zook and Leddy[15] examined the density and solubility of recast, annealed, and commercial Nafion® membranes. They found that unheated recast membranes were found to be ∼ 20% less dense in water than both commercial membranes and recast membranes heated at 140°C for 40, 50, and 60 min. But they did not discuss the macro properties of the membranes such as conductivity and methanol permeability. Annealed solution-cast membranes were also mentioned by Gebel et al.[16] But, only the micro structure was examined, the change of the macro properties was not mentioned. Sone et al.[17] studied the conductivity of H^+-type Nafion 117 membrane before and after heat-treatment at 80, 105, and 120°C, respectively. They found that heat-treatment of

membrane decreased the conductivity due to the change in its structure. When Nafion® 117 membrane was heat-treated over 80°C, some of the micropores in the membrane were attached to each other, and some were closed by the thermal treatment. The shrinkage of the membrane caused a lower water content and conductivity. In their work, the effect of heat-treatment on conductivity and water content was measured on Nafion® 117, which was melt-extruded from PFSI precursor. Solution-cast membranes were not mentioned in their work. Also in Sone's work, the highest heat-treatment temperature was 120°C, properties of the membranes heat-treated at higher temperatures was unknown. Now we know that the morphology of a melt-extruded membrane is different from that of a solution-cast membrane.[16] Gebel et al. proposed that the membrane reconstructed at room temperature may be considered to be "a compact nearly dried solution," meaning that only small rearrangements and small reentanglements occurred, not enough to prevent room-temperature dissolution in numerous polar solvents.[16] On the other hand, annealing led to large structural modifications with entanglements and crosslinks preventing dissolution.

Silva et al.[18] reported that the conductivity performance of membranes cast from N,N-dimethyl formamide (DMF)-based solutions was comparable to that of Nafion® 112 and 115. We found that membranes prepared from solutions with DMF as the solvent at 150°C can easily disintegrate into granules in DMF at 90°C. The granules were linked by weak intermolecular force, which could be destroyed easily in hot aprotic polar solvent such as DMF. Annealing is a useful way to change the microstructure of the membranes.[9,15,16] Unfortunately, the published work does not give enough information about the macroscopic properties of the annealed solution-cast membranes at high temperatures, such as proton conductivity and methanol permeability.

In this study, we prepared solution-cast perfluorosulfonated membranes with DMF as the solvent, and then annealed the membranes at different temperatures from 150 to 230°C. Measurements of X-ray diffraction (XRD), small angle X-ray scattering (SAXS), proton conductivity, and methanol permeability etc. were used to evaluate the annealed membranes.

EXPERIMENTAL

Materials

Along with PFSI, the following chemicals were also used: DMF, NaOH, NaCl, H_2O_2, and HCl. Before use, DMF was dried and distilled twice under reduced pressure. All other reagents were used as received without further purification. Tetrafluoro-

ethylene and perfluoro [2-(2-fluorosulfonylethoxy) propyl vinyl ether] were synthesized in Shandong Dongyue Polymer Materials (Zibo, China), the purity was more than 99.99%.
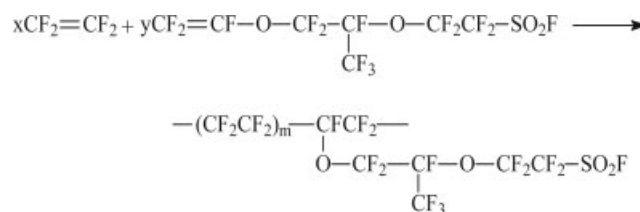
Perfluorosulfonated ionomer preparation

Perfluorosulfonated precursor was synthesized by copolymerization of tetrafluoroethylene and perfluoro [2-(2-fluorosulfonylethoxy) propyl vinyl ether] in fluorocarbon solvent with perfluoroacyl peroxide initiator, as shown in Scheme 1. After the copolymerization, the precursor with functional group of $-SO_2F$ was separated, rinsed, and dried. Then the precursor was added to 29 wt % aqueous sodium hydroxide solution and refluxed at 100°C for 48 h to chemically convert the $-SO_2F$ groups to $-SO_3Na$ groups. Afterward, the PFSI was washed with deionized water and dried under vacuum at 80°C for 12 h.

Solution-cast PFSI membranes preparation

PFSI membranes were prepared from 21 wt % PFSI/DMF solution. Na^+-type PFSI was dissolved in DMF, using an autoclave at 230°C for 4 h.[10,19] The solution was then transferred into a rotary vacuum evaporator to obtain a solution of 21 wt % concentration. The concentrated solution was put in a vacuum oven at 40°C for 12 h to get rid of small air bubbles and then poured into a cleaned glass mold. The mold was kept at 125°C with a steady air stream for 1 h, and then kept at 125°C and 1 mbar for 45 min to remove the solvent thoroughly. A pristine film with about 50 μm thickness was watered and peeled intact from the mold.

Annealing process: Annealing was carried out in a vacuum oven. The pristine wet film was cut into pieces and annealed at different temperatures respectively. The oven was heated to the desired temperature and kept for 1.5 h, after that the heater was turned off and the oven slowly cooled down to room temperature over a 3 ~ 4 h period.

$$xCF_2{=}CF_2 + yCF_2{=}CF{-}O{-}CF_2{-}\underset{\underset{CF_3}{|}}{CF}{-}O{-}CF_2CF_2{-}SO_2F \longrightarrow$$

$$-(CF_2CF_2)_m{-}\underset{\underset{\underset{\underset{CF_3}{|}}{CF}}{|}}{\underset{O{-}CF_2{-}}{CFCF_2}}{-}O{-}CF_2CF_2{-}SO_2F$$

Scheme 1 Synthesis of perfluorosulfonated precursor with tetrafluoroethylene and perfluoro [2-(2-fluorosulfonyl-ethoxy) propyl vinyl ether], m is about 5 ~ 7.

Membrane characterization

The ion exchange capacity of the PFSI was determined by titration to be 0.95 mequiv/g.

Water content of fully hydrated H^+-type PFSI membranes was measured by boiling the membrane samples in deionized water for 1 h, and then the samples were taken out, wiped with filter-paper swiftly and immediately weighed on a microbalance. Dry weight of the samples was measured directly after the samples were desiccated at 1 mbar and 80°C for 24 h. The amount of water content (W_{H_2O}) of the membranes was calculated from

$$W_{H_2O} = \frac{M_{wetmem} - M_{drymem}}{M_{drymem}} \times 100\% \qquad (1)$$

where M_{drymem} and M_{wetmem} are the weights of dry and corresponding water-boiled samples, respectively.

Voluminal expansion of the membranes (E_{vol}) is calculated according to the volumes of the dry and wet membranes as follows:

$$E_{vol} = \frac{V_{wetmem} - V_{drymem}}{V_{drymem}} \times 100\% \qquad (2)$$

where V_{drymem} and V_{wetmem} are the volumes of dry membrane and corresponding water-boiled membrane, respectively.

X-ray diffraction measurement

X-ray diffraction (XRD) studies were conducted on dry, Na^+-type annealed membrane samples, with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and a Cu Kα radiation source (λ = 0.15, 418 nm), at a scanning rate of 2°/min. X-ray tube voltage and current were set at 40 kV and 30 mA, respectively.

Small angle X-ray scattering measurement

To obtain X-ray diffusion results from swollen hydrolyzed membrane samples, methods were developed to inhibit samples dehydration during the course of the experiments. This was achieved by sealing the sample in a bag constructed from oriented polypropylene film that possesses low permeability to water and is also "transparent" in the small angle X-ray scans.

Small-angle X-ray scattering (SAXS) experiments were carried out using a Bruker general area detector diffraction system. Cr Kα1 radiation (λ = 2.2897E) was used as an incident beam with the anode generator operated at 30 mA and 25 kV. A three-pinhole system was used to collimate the X-ray

beams along with graphite monochromator to control the incident X-ray beams on the sample. The sample to detector distance was 30 cm in length. Wet H^+-type PFSI membranes were used. Scattering data for all samples were background subtracted and corrected for absorption.

Proton conductivity measurement

Before proton conductivity measurement, the annealed membranes were first boiled in a 3% H_2O_2 aqueous solution for 1 h, rinsed in boiling deionized water repeatedly, immersed in 10% HCl for 12 h, rinsed again in deionized water, and finally boiled in deionized water for 1 h. After this treatment, the membranes were stored in deionized water.

Proton conductivity of membranes in normal direction was measured at 25°C and 100% relative humidity by pressing the H^+-type samples in a custom-made measurement cell, which consisted of a cylinder made of insulating PTFE material and two electrodes made of stainless steel. The electrode surfaces were gilded and kept clean to avoid any contact resistance during measurements. The membrane to be tested was placed between the flat upper and lower electrodes. The electrodes were connected through copper wires to an impedance/gainphase analyzer (Solatron Analytical, Model Solatron 1260, UK) in combination with an electrochemical interface (Solatron Analytical, Solatron 1287, UK). The resistance value associated with the membrane conductivity was determined from the high frequency intercept of the impedance with the real axis.

The conductivity σ was calculated from following equation:

$$\sigma = \frac{d}{RS} \qquad (3)$$

where d and S denote the thickness of the membrane and the area of the membrane contact to the electrodes, respectively, and R is the resistance of the membrane.

Methanol permeability measurement

A custom-made side-by-side liquid diffusion cell (Fig. 1) was used to measure the methanol permeability using the procedure reported elsewhere.[20–22] The cell consisted of two compartments each ∼ 28 mL, which were separated by a vertical membrane. Donor compartment A of the cell was filled with 26 mL methanol (8 vol %) in deionized water as feed solution, and receptor compartment B was initially charged with 26 mL deionized water. Both compartments were magnetically stirred during the permeation experiment at 25°C. A methanol flux
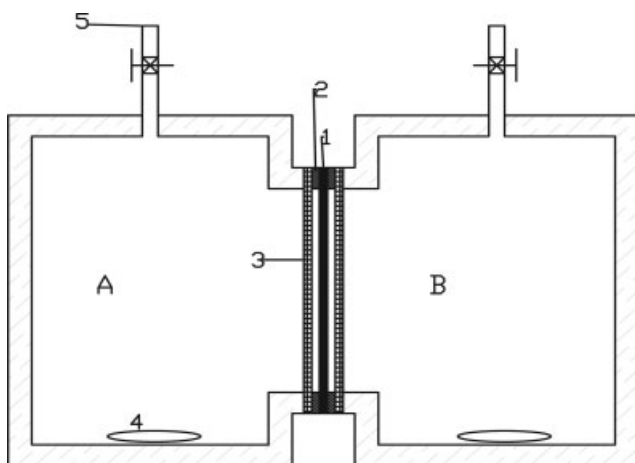
Figure 1 Schematic drawing of the diffusion cell: (1) PFSI membrane; (2) silastic gasket; (3) stainless steel net; (4) magnetic stirrer; (5) sample port. Compartment A is initially water-methanol mixture, while compartment B is pure water.
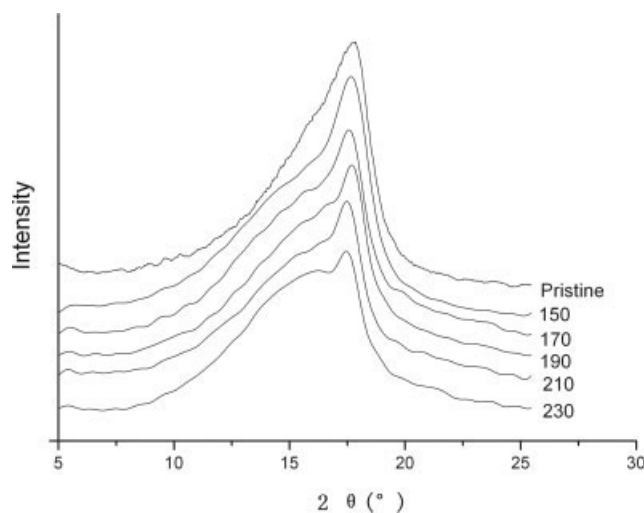

Figure 2 X-ray diffraction profiles of the pristine membrane and the membranes annealed at 150, 170, 190, 210, 230°C, respectively. All samples were dry Na$^+$ type. The numbers besides the curves are the corresponding annealing temperature.

was established across the membrane owing to the concentration difference between the two compartments. The methanol concentration of the receptor compartment C_B was measured versus time by gas chromatography with a thermal conductivity detector (Fuli, model GC9790-Π, China). The temperature was kept constant in a thermostatic water bath.

Methanol permeability can be determined with the use of a pseudosteady-state solution of diffusion in plane sheet geometry. The methanol permeability, P, is calculated from the slope of the straight-line plot of methanol concentration versus permeation time. The methanol concentration in the receptor compartment as a function of time is given by

$$C_B(t) = \frac{A}{V_B}\frac{P}{L}C_A t \qquad (4)$$

where C_A and C_B are methanol concentrations in compartment A and B, respectively, A and L are the membrane area and thickness, respectively, V_B is the liquid volume in compartment B, and t is time.

RESULTS AND DISCUSSION

XRD measurement

Figure 2 shows XRD data for the pristine membrane and five membranes annealed at different temperatures. All the membranes display a broad diffraction feature at $2\theta = 8$–$25°$, which can be deconvoluted into two peaks. The broad scattering peak at $2\theta \approx 15.5°$ and the sharp peak at $2\theta \approx 17.5°$ are assigned, respectively, to diffraction maxima associated with amorphous and crystalline regions of the membranes.[23] A sample XRD spectrum including fit-

ted amorphous and crystalline peaks is shown in Figure 3. The weight-average crystallinity "W_{cr}" was calculated from eq. (5). W_{cr} and FWHM (full-width at half maximum) of the crystalline peak are listed in Table I.

$$W_{cr} = \int_0^\infty I_{cr}(s)s^2 ds / \int_0^\infty [I_{cr}(s) + I_{am}(s)]s^2 ds \qquad (5)$$

where W_{cr} is the calculated crystallinity, I_{cr} and I_{am} are the relative intensities of the crystalline and amorphous peaks, respectively.
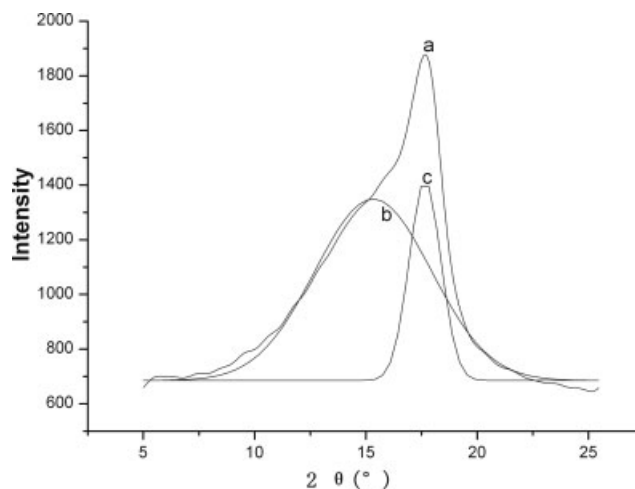

Figure 3 X-ray diffraction profiles of perfluorosulfonic membrane annealed at 150°C. Curve a (measured data) is deconvoluted to provide fitted curve b (amorphous region at $2\theta \approx 15.5°$) and curve c (crystalline peak at $2\theta \approx 17.5°$).

TABLE I
Weight-Average Crystallinity and FWHM of the Crystalline PEAK of the Pristine and Annealed Membranes

Annealing temperature (°C)	Weight-average crystallinity (%)	FWHM (°)
Pristine membrane	22.0	1.56
150	14.2	1.42
170	13.3	1.12
190	12.7	1.06
210	11.6	1.04
230	7.4	0.95

As seen from Figure 2 and Table I, with increasing annealing temperature, the sharp peak looses its intensity while the broad peak is enhanced as a consequence of decreasing X-ray crystallinity. Moreover, FWHM decreases, indicating that the perfection of the crystals becomes high with increasing annealing temperature. DSC curves for Nafion® membranes displayed two endothermic peaks, at 120–150°C and near 230°C.[24,25] Page et al.[26] proposed that the high-temperature peak was attributed to melting of PTFE-like crystallites in the presence of an electrostatic network, while the low-temperature peak was due to the melting of small, imperfect crystallites. In our experiment, the annealing temperature is higher than 150°C, which may cause the small imperfect crystallites to melt and the side chains to move freely. The free movement of the side chains could facilitate the sulfonic groups to form new ionic clusters, and simultaneously it could disrupt the rearrangement of the main chain segments to form new crystallites. After the melting of the crystalline region, at the temperatures lower than the melting point of pure PTFE (327°C), it is difficult for the melting imperfect crystal to form a new perfect one with the disruptive effect of the side chains on the lamellar ordering of the tetrafluoroethylene backbone segments.[27] So the intensity of the crystalline peak and the crystallinity decrease as the annealing temperature increases, as shown in Figure 2 and Table I.

SAXS measurement

Figure 4 presents SAXS curves for the pristine and annealed membranes. The result was obtained in wet H^+-type state. The scattering maximum at $2\theta \approx 2.2°$ was assigned to the ionic cluster of the membranes.[23]

Membranes annealed at 150 and 170°C and the pristine membrane hardly show ionic scattering maximum. We propose that it is not due to the absence of clusters because the membranes can transfer protons very well, but rather simply due to the small electron density difference between the clusters and the surrounding medium, because in these mem-

branes, only "loose clusters" are formed. The sulfonic acid groups did not interact strongly with each other with a disruptive effect from polymer backbones and side chains. Some of them were even separately buried in chain segments. When annealed at low temperatures, the molecular chains in the membrane had only low energy, not all the buried sulfonated groups could move freely out of the cages of the backbone and the side chains. At higher temperatures over 190°C, higher energy enabled the end groups of the side chains to move out of the cages to aggregate together with electrostatic force to form clusters. Simultaneously, there existed a molecular rearrangement in the clusters with a high mobility of the chain segments. More highly organized "compact clusters" were expected in the annealed membranes with increasing temperature. So the membranes annealed at 190, 210, and 230°C show increasing scattering maximum with annealing temperature. Also we can find in Figure 4 a slight shift of the ionic scattering maximum toward smaller 2θ with increasing annealing temperature, indicating that larger clusters formed in the membranes.

Proton conductivity and water content

Proton conductivity of solution-cast perfluorosulfonated membranes was considerably affected by annealing. Table II shows the result of proton conductivity of the pristine and annealed membranes at 25°C and relative humidity (RH) of 100%. From the table, we can see that proton conductivity increases with increasing annealing temperature. It means that the ionic channels in the membranes were changed into more unblocked structure after being annealed
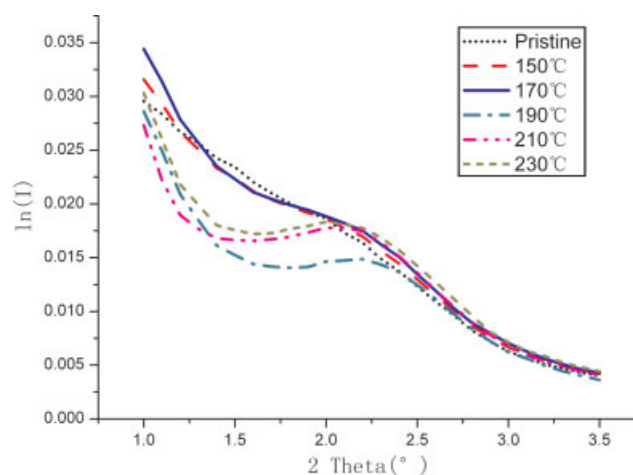

Figure 4 SAXS curves for the pristine membrane and membranes annealed at 150, 170, 190, 210, 230°C, respectively. All samples were wet H^+ type. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
**Conductivity, Water Content, Voluminal Expansion, and Voluminal Water Content of
the Pristine and Annealed Membranes**

Annealing temperature (°C)	Conductivity (mS/cm)	Water content (%)	Voluminal expansion (%)	Voluminal water content (g/cm^3)
Pristine membrane	23.86	45.47	90.60	0.446
150	24.91	42.38	80.20	0.450
170	25.33	40.64	72.71	0.452
190	28.82	39.28	63.62	0.457
210	31.82	38.96	55.17	0.465
230	32.23	37.80	47.62	0.471

at increasing temperature. As discussed earlier, with increasing annealing temperature, higher energy enabled the buried separate sulfonated groups to move out of the cages of backbones and side chains to aggregate together with electrostatic force to form clusters. Simultaneously, free movement of the side chains led to more organized clusters. Annealing at higher temperature freed more buried sulfonated groups, the ionic pathway through which the protons can pass expanded, so the proton conductivity of the membranes increased accordingly.

Water content of the annealed membranes decreased with increasing annealing temperature, indicating the change of the microstructure of the membranes. Michael Falk[28] studied infrared spectra of perfluorosulfonated polymer and of water in perfluorosulfonated polymer. They found that water interacts with both the sulfonic groups and the fluorocarbon segments. When the membranes were annealed at low temperatures, loose clusters formed, much of the water absorbed around the sulfonic groups interacted strongly with the fluorocarbon segments, and some of them even occupied the free volume among the hydrophobic zone. Heat-treatment at higher temperature set free more free volume in the membrane and made the molecular segments more compact. Accordingly it is hard for water to infiltrate into the hydrophobic zone and water content and volume expansion decreased with increasing annealing temperature.

Water content is an important factor involved with membrane conductivity. Sone et al.[17] proposed that there existed micropores in the membrane, which were attached to each other and some could be closed by thermal treatment. The shrinkage of the membrane caused a lower water content and conductivity. But in their work the thermal treatment temperature was lower than 120°C, which could not bring about the rearrangement of the sulfonated groups. And it is important that the membranes in their work were not boiled in water. Water is important for proton transfer, but higher water content does not mean higher conductivity. We propose that conductivity of the membranes is more relative to

average water density in the membranes. Here we use a parameter V_{H_2O} to denote the voluminal water content. It means the weight of water in per unit volume of wet membrane. It is calculated as follows.

$$V_{H_2O} = \frac{M_{H_2O}}{V_{wetmem}} = \frac{M_{wetmem} - M_{drymem}}{V_{wetmem}} \quad (6)$$

where M_{H_2O} is the weight of water in wet membrane, V_{wetmem} is the volume of wet membrane, and M_{wetmem} and M_{drymem} are the weights of wet membrane and the corresponding dry membrane.

Voluminal water content of the membranes is listed in Table II. Although water content decreases with increasing annealing temperature, voluminal water content increases. The wet membranes annealed at higher temperature have more water in per unit volume. Also we can find that the voluminal expansion of the membranes decreases with increasing annealing temperature, it means that the membranes shrink due to the heat-treatment. The average distance of water molecules and sulfonated groups in such membranes decreased, which facilitated the transfer of the protons, so it is natural that proton conductivity of the annealed membranes
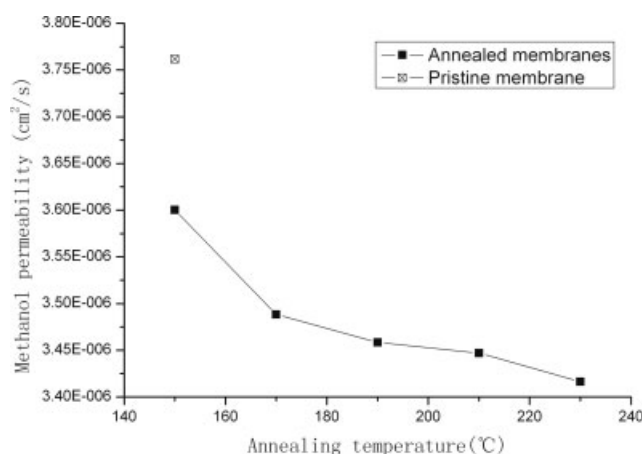

Figure 5 Methanol permeability of the pristine and annealed membranes.

increases with increasing annealing temperature, in spite of the decrease of water content.

Methanol permeability

In the present study, the annealing effect on the permeation of methanol molecules through the annealed membranes was also considered. Figure 5 shows the methanol permeability as a function of annealing temperature. Unlike the effect on the conductivity, annealing decreased the methanol permeability of the perfluorosulfonated membranes slightly, which was similar to the water content of the sample membranes.

Methanol can crossover the perfluorosulfonated membranes not only through the ionic channels, but also it can crossover the membranes among the hydrophobic perfluorinated matrix.[20] Annealing at higher temperature induced more compact structure of the backbone and the side chains in the wet membranes, which reduced the hydrophobic channel of the methanol molecules. Although higher annealing temperature expanded the overall ionic channels; simultaneously it decreased the free volume among the hydrophobic zone. The total path through which methanol can crossover the membrane was reduced slightly, and then the methanol permeability of the annealed membranes decreased as a result.

CONCLUSIONS

In this work, micro structure and macro properties such as proton conductivity and methanol permeability of perfluorosulfonated membranes annealed at different temperatures were investigated. Annealing changed the micro morphology of the membranes. The crystallinity of the membranes decreased and more compact clusters formed with increasing annealing temperature. Simultaneously, the macro properties such as water content, proton conductivity, and methanol permeability changed as well. Annealing increased proton conductivity of the membranes, because heat-treatment set free the sulfonic acid groups that were buried in the backbone and side chains, and more compact clusters formed. Methanol permeability and water content decreased with increasing annealing temperature, this may be due to the denser structure of the membranes annealed at higher temperature.

References

1. Carla, H. W. J Membr Sci 1996, 120, 1.
2. Eisenberg, A.; Yeager, H. L.; Perfluorinated Ionomer Membranes; American Chemistry Society: Washington, DC, 1982; p 1.
3. Shukla, A. K.; Ravikumar, M. K.; Gandhi, K. S. J Solid State Chem 1998, 2, 11.
4. Scott, K.; Taama, W.; Cruickshank, J. J Appl Electrochem 1998, 28, 289.
5. Ren, X. M.; Springer, T. E.; Zawodzinski, T. A.; Gottesfeld, S. J Electrochem Soc 2000, 147, 466.
6. Heinzel, A.; Barragan, V. M. J Power Sources 1999, 84, 70.
7. Kreuer, K. D. J Membr Sci 2001, 185, 29.
8. Kauranen, P. S.; Skou, E. J Electroanal Chem 1996, 408, 189.
9. Moore, R. B.; Martin, C. R., III. Anal Chem 1986, 58, 2569.
10. Grot, W. G. U. S. Pat. 4,433,082 (1984), du Pont de Nemours, E. I., and Co., USA.
11. Rubinstein, I.; Bard, A. J. J Am Chem Soc 1980, 102, 6641.
12. Rhee, C. H.; Kim H. K.; Chang, H.; Lee, J. S. Chem Mater 2005, 17, 1691.
13. Silva, R. F.; Passerini, S.; Pozio, A. Electrochim Acta 2005, 50, 2639.
14. Laporta, M.; Pegoraro, M.; Zanderighi, L. Macromol Mater Eng 2000, 282, 22.
15. Zook, L. A.; Leddy J. Anal Chem 1996, 68, 3793.
16. Gebel, G.; Aldebert, P.; Pineri, M. Macromolecules 1987, 20, 1425.
17. Sone, Y.; Ekdunge, P.; Simonsson, D. J Electrochem Soc 1996, 143, 1254.
18. Silva, R. F.; De Francesco, M.; Pozio, A. Electrochim Acta 2004, 49, 3211.
19. Charles, R. M.; Teresa, A. R.; James, A. F. Anal Chem 1982, 54, 1639.
20. Tricoli, V. J Electrochem Soc 1998, 145, 3798.
21. Chang, H. Y.; Lin, C. W. J Membr Sci 2003, 218, 295.
22. Tricoli, V.; Carretta, N.; Bartolozzi, M. J Electrochem Soc 2000, 147, 1286.
23. Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1981, 14, 1309.
24. De Almeida, S. H.; Kawano, Y. J Therm Anal Calorim 1999, 58, 569.
25. Moore, R. B.; Martin, C. R., III. Macromolecules 1988, 21, 1334.
26. Page, K. A.; Cable, K. M.; Moore, R. B. Macromolecules 2005, 38, 6472.
27. Howard, W. S. Jr. Macromolecules 1982, 15, 320.
28. Falk, M. Perfluorinated Ionomer Membranes; Eisenberg, A.; Yeager, H. L.; Ed.; ACS Symposium Series 180; American Chemistry Society: Washington, DC, 1982; p 139.