*Transactions of the Materials Research Society of Japan* 30[4] 943-946 (2005)

# Proton Conduction Properties of Crosslinked PTFE Electrolyte Membranes with Different Graft-chain Structures

S. Sawada[a], T. Yamaki[b]*, M. Asano[b], T. Terai[c], M. Yoshida[b]
[a]Graduate School of Engineering, The University of Tokyo,
2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan
[b]Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute (JAERI),
1233 Watanuki, Takasaki, Gunma 370-1292, Japan
*Fax: 027-346-9617, tetsuya@taka.jaeri.go.jp
[c]Nuclear Engineering Research Laboratory, Graduate School of Engineering, The University of Tokyo,
2-22 Shirakata Shirane, Tokai-mura, Naka-gun, Ibaraki 319-1188, Japan

We synthesized crosslinked-polytetrafluoroethylene (PTFE) electrolyte membranes by a radiation grafting technique under different conditions, and then investigated their proton conduction properties at controlled temperatures and relative humidities (R.H.) by using an AC impedance method. The density and length of graft chains were controlled by varying the pre-irradiation dose and grafting time, respectively. When the pre-irradiation dose was fixed at 15 kGy to make the graft chains an uniform density, the elongation of the graft chains increased the ion exchange capacity (*IEC*), thereby enhancing their proton conductivity. The membrane with an *IEC* of 2.8 meq $g^{-1}$ possessed the maximum conductivity reaching 0.20 S $cm^{-1}$ at 80 ℃ and R.H. 95%. At almost the same *IEC*, membranes with more and shorter graft chains showed higher conductivity compared to those with less and longer chains. This result was probably related to the different structures of hydrophilic domains as proton-conducting pathways.

Key words: Polymer Electrolyte Fuel Cell, Crosslinked PTFE, Polymer Electrolyte Membrane, Proton Conductivity, Radiation-graft Polymerization

## 1. INTRODUCTION

During the past decade, polymer electrolyte fuel cells (PEFCs) have been expected to be used for vehicle and other applications because of their high-efficient power generation [1]. The principal component of PEFC is the proton exchange membrane (PEM) that prevents the mixing of the reactant gases and transports protons from the anode to cathode. At present, the most widely used PEM is Dupont's Nafion, which consists of a polytetrafluoroethyrene (PTFE) backbone with pendant side chains of perfluorinated vinyl ethers terminated by sulfonic acid groups [2]. Nafion has excellent properties, but is still too expensive owing to the complicated production process, which fails to spread widely.

One of the most important properties of PEMs is proton conductivity which directly affects the output power density of PEFC [3]. Transport of protons is strongly dependent on the hydrated state of the membrane. In electrolyte membranes, absorbed water molecules probably aggregate around the ion exchange groups by attractive interactions to comprise the hydrophilic domains as proton conducting pathways. According to Gierke et al [4], for example, the hydrophilic domains in Nafion containing water and the sulfonic acid groups consist of connected clusters with a diameter of 3-5 nm. Such an unique structure is believed to be the origin of its high proton conductivity [5].

As alternatives to Nafion, in recent years, there have been much interest in developing new materials with high proton conductivity, good mechanical strength, and chemical stability. The most promising as these materials are PEMs synthesized by a convenient and low cost radiation grafting method. In this method, a fluoropolymer film is irradiated and then grafted with styrene, and finally polystyrene grafts are sulfonated. Quite recently, T. Yamaki et al. have carried out the radiation-induced grafting of styrene into crosslinked PTFE films and subsequent sulfonation [6,7]. This was the first example of polystyrene sulfonic acid (PSSA) containing PEM with crosslinked fluoropolymer main chains that Nafion never has. Various synthesizing conditions of this novel electrolyte membrane diversify the molecular structures, and enable us to vary arbitrarily the ion exchange capacity (*IEC*) up to 3.0 meq $g^{-1}$, which is far larger than that of Nafion. Therefore, there is a possibility of controlling their proton conductivity in a wide range.

In this study, we investigated the influence of the PSSA graft-chain structures on the proton conductivity of the crosslinked PTFE electrolyte membranes. The density of the graft chains was controlled by pre-irradiation dose while chain length was varied by grafting time. Their proton conduction properties were then examined by using an AC impedance technique at controlled temperatures and relative humidities (R.H.). The obtained results were explained based on the different structures of hydrophilic domains. This paper reports for the first time that the conductivities of the membranes were determined by not only IEC but also graft-chain structures.

## 2. EXPERIMENT

### 2.1 Synthesis of electrolyte membranes

We used a 42-$\mu$m thick film of 100-kGy crosslinked PTFE as a base material. The film was irradiated with 15 or 60-kGy $\gamma$-rays in a grass ampoule filled with Ar at room temperature. The irradiated films were immediately immersed in a styrene monomer (deaerated by Ar bubbling before use), where they were kept for 9-72 hours at 60 ℃. In this pre-irradiation method, graft polymerization of monomers starts from the radicals generated by the γ-ray irradiation and the polymer chains grow during the course of the reaction. Thus, the γ-ray pre-irradiation dose and grafting time will control the density and length of the graft chains, respectively.

After the grafting reaction, the films were taken out from the ampoule and extracted with toluene to remove any excess styrene. The grafted films were then dried in a vacuum at 50 ℃ to a constant weight. The degree of grafting (*DOG*) was defined as follows:

$$DOG\,(\%) = \frac{W_g - W_o}{W_o} \times 100$$

where $W_o$ and $W_g$ are the weights of original and grafted films, respectively.

For sulfonation, the grafted films were immersed in a 0.2 mol dm$^{-3}$ chlorosulfonic acid/1,2-dichloroethane mixture at 50 ℃ for 6 hours. Finally, the resulting membranes were rinsed with pure water and then dried in a vacuum oven.

### 2.2 *IEC*

The membrane samples in an acid form were equilibrated in a 3 mol dm$^{-3}$ NaCl solution for 6 hours at 50 ℃. The solution containing protons released from the membrane was titrated with a standardized 0.1 mol dm$^{-3}$ NaOH solution by an automatic titrator until pH 7 was reached. From the volume of the NaOH solution consumed in titration, the amount of protons in the membrane was determined, and the *IEC* (meq g$^{-1}$) was evaluated by:

$$IEC = \frac{1000 \times N_s}{W_d}$$

where $N_s$ and $W_d$ are the number of the sulfonic acid groups (mol) and the weight of the dried electrolyte membrane, respectively.

### 2.3 Water uptake

The water uptake was investigated in a chamber controlled at temperatures of 30-80 ℃ and R.H. of 50-95%. After equilibration for about 2 hours, the membrane was taken out from the chamber and weighted. From the weight difference between the membranes in dried and hydrated states, the mass of absorbed water was calculated, and finally a water content parameter, λ, was estimated by:

$$\lambda = \frac{N_W}{N_S}$$

where $N_W$ and $N_S$ are the numbers of water molecules and sulfonic acid groups, respectively.

### 2.4 Conductivity measurement

The conductivity of the membranes was determined by a two-probe AC impedance technique using a measurement cell made of Teflon. The membrane samples cut into 1.0 cm strips were clamped between two platinum electrodes in the cell. The cell was placed in a thermo-controlled humidified chamber at different temperatures (30-80 ℃) and R.H. (50-95%). The measurements were performed using a frequency response analyzer (Solartron SI 1255B), connected to an electrochemical interface (Solartron SI 1287), with an AC amplitude of 100 mV over the frequency range of 10$^3$-10$^6$ Hz. The diameter of the semicircle observed in the cole-cole plot corresponds to the membrane resistance, so the membrane conductivity was calculated by the following equation:

$$\sigma = \frac{l}{RS}$$

where $\sigma$, $l$, $R$, and $S$ are the proton conductivity (S cm$^{-1}$), the distance between the two electrodes, the membrane resistance, and the cross-sectional area of the membrane, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Membranes

The grafting conditions as well as *DOG*s and *IEC*s of the synthesized membranes are given in Table 1. On going from sample (a) to (d), graft-chain length was extended, therefore their *DOG*s and *IEC*s increased from 30 to 84% and from 1.7 to 2.8 meq g$^{-1}$, respectively. These samples are considered to possess the same density chains because the pre-irradiation dose was stable at 15 kGy. On the other hand, sample (e) included more and shorter chains compared to sample (d). This is because it was prepared by higher pre-irradiation dose and shorter grafting time although both the samples had almost the same *IEC*s.

**Table 1.** Grafting conditions and membrane properties.

| sample | pre-irradiation dose (kGy) | grafting time (hours) | *DOG* (%) | *IEC* (meq g$^{-1}$) |
|---|---|---|---|---|
| (a) | 15 | 9 | 30 | 1.7 |
| (b) | | 24 | 42 | 2.1 |
| (c) | | 48 | 71 | 2.6 |
| (d) | | 72 | 84 | 2.8 |
| (e) | 60 | 24 | 79 | 2.7 |

Fig. 1 shows plots of λ, the number of water molecules per sulfonic acid group, as a function of the *IEC* of samples (a)-(d) at 80 ℃, and R.H. 80 and 95%. λ was enhanced at higher R.H. where the samples absorbed much water from more humidified atmosphere. However, this did not change greatly over a wide range of *IEC*s. The present result was very striking because this trend was completely different from that observed in other PEMs such as the BAM series of membranes based on α,β,β-trifluorostyrene, DAIS membranes based on sulfonated styrene-(ethrene-butyrene)-styrene triblock copolymers, and so on. These membranes became easy to absorb water and swell largely in the high *IEC* region, and as a result λ jumped remarkably. For example, in the DAIS membrane, when the *IEC* increased from 0.94 to 1.71 meq $g^{-1}$, λ rose by six times [8]. Generally speaking, absorption of much water causes mechanical strength of the membranes to be reduced. In our case, the use of the crosslinked PTFE films as base materials restrained the water absorption, which should enhance the mechanical stability.

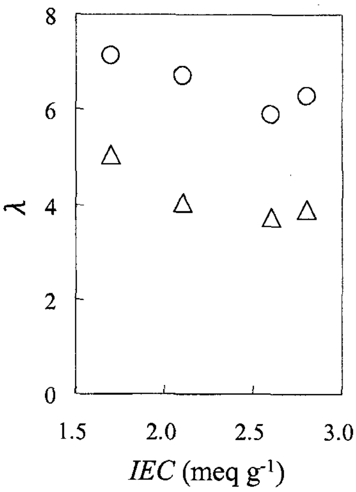

**Fig. 1.** Plots of λ versus *IEC* for samples (a)-(d) at 80 ℃. This figure also compares the results at R.H. 80 (△) and 95% (○).

3.2 Proton conductivity

Fig. 2 shows plots of the conductivity versus the *IEC* of samples (a)-(d) at 80 ℃, and R.H. 80 and 95%. The higher R.H. was, the higher conductivity all the samples showed. This is due to the expansion of the hydrophilic domains promoting the mobility of protons. The sample with a larger *IEC* became more conductive; the membrane with an *IEC* of 2.8 meq $g^{-1}$ possessed the maximum conductivity reaching 0.20 S $cm^{-1}$ at 80 ℃ and R.H. 95%. This was higher than that of Nafion (0.13 S $cm^{-1}$ at the same environments).

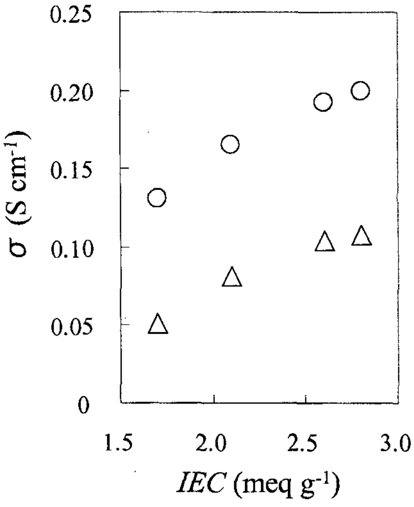

**Fig. 2.** Plots of σ versus *IEC* for samples (a)-(d) at 80℃. This figure also compares the results at R.H. 80 (△) and 95% (○).

However, large *IEC* does not always increase the conductivity, because this occasionally accompanies excessive swelling of the membranes which dilutes the concentration of protons and decreases the proton conductivity. On the contrary, in the crosslinked PTFE electrolyte membrane, water sorption was remarkably restricted even if the *IEC* was large as described above. Consequently, it was suggested that such a dimensional stability maintained the high proton concentration to enhance the proton conductivity.

Next, the temperature dependence of the proton conductivity was investigated by applying an Arrhenius expression as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)$$

where $\sigma$, $\sigma_0$, $E_a$, $R$, and $T$ are the proton conductivity, the pre-exponential factor, the constant activation energy for proton conduction, the gas constant, and the absolute temperature, respectively. If a straight line is drawn through the points in the plot of ln $\sigma$ and $1/T$, the value of $E_a$ is estimated from the slope of the line.

Fig. 3 shows plots of ln $\sigma$ at R.H. 95% as a function of $1/T$ for samples (a)-(d). The conductivity of all the samples obeyed the Arrhenius law. The slope of fitted line became gentler when going from sample (a) to sample (d). This indicates that the activation energy decreased as an ionic content was raised.

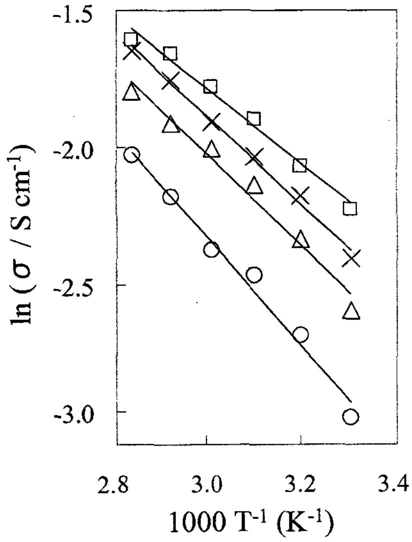

**Fig. 3.** Arrhenius plots of σ for sample (a) (○), (b) (△), (c) (×), and (d) (□). The R.H. was 95%.

Fig. 4 shows the Arrhenius plots of proton conductivity at R.H. 80%. For samples (c) and (d), plots deviated from linearity, and the approximation was not valid. This suggests that there might be at least two proton conduction mechanisms in the different temperature regions, where the structures of the hydrophilic domains are varied.

Fig. 5 compares the Arrehenius plots for samples (d) and (e) at R.H. of 80 or 95%. At 95%, the conductivities and activation energies of both the membranes were nearly equal at every temperature. On the other hand, at

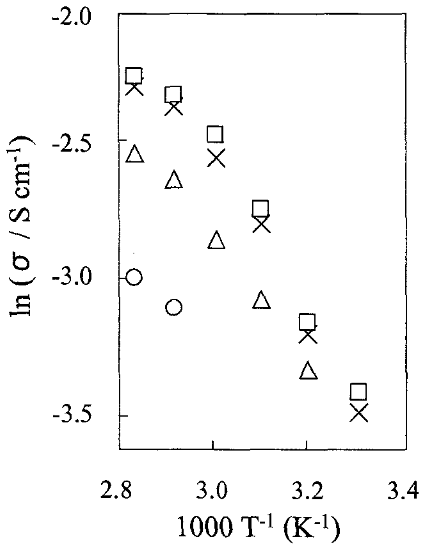

**Fig. 4.** Arrhenius plots of $\sigma$ for sample (a) (○), (b) (△), (c) (×), and (d) (□). The R.H. was 80%.

R.H. 80%, the conductivity of sample (e) exceeded that of sample (d). The Arrhenius type temperature dependence appeared only for sample (e). These results are rationalized by considering the structures of hydrophilic domains formed by the PSSA graft chain and water, as in the following.

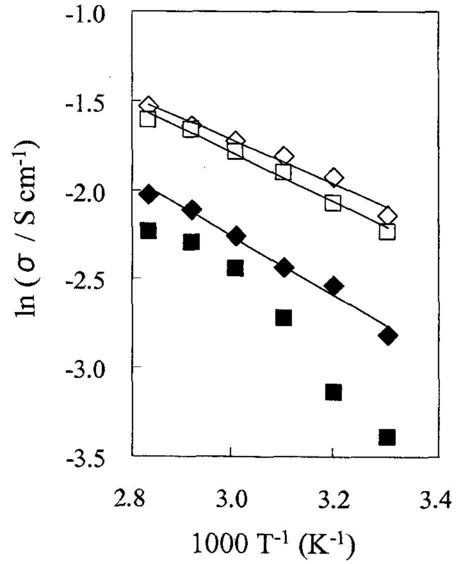

**Fig. 5.** Arrhenius plots of $\sigma$ for sample (d) (□; ■) and (e) (◇; ◆). This figure compares the results at R.H. 80 (filled) and 95% (open).

Fig. 6 schematically illustrates the models of possible hydrophilic domains in the membranes with different graft-chain structures. The hydrophilic domains as proton conducting pathways are probably formed along the PSSA graft chains by absorbing water. As shown in (A), the hydrophilic domains in sample (d) are isolated from each other because graft chains are sparsely attached by the low pre-irradiation dose. In contrast as shown in (B), sample (e) has the hydrophilic domains connected well because of the high-density graft chains. As R.H. is increased, the hydrophilic domains grow large enough to connect each other even in (d); the graft-chain structure is not a significant factor determining the conductivity. From these models, therefore, it is concluded that the PSSA graft-chain structures affect the proton conduction properties.

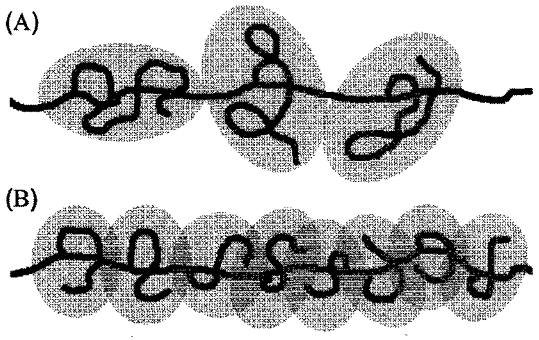

**Fig. 6.** Possible models of the hydrophilic domains in the membranes with different graft-chain structures; (A) less and longer chains; (B) more and shorter chains.

## 4. CONCLUSIONS

The effect of graft-chain structures on the proton conductivity of radiation-grafted electrolyte membranes based on crosslinked PTFE films was studied. The membranes with graft chains of different density and length were synthesized by controlling the grafting conditions such as pre-irradiation dose and grafting time. The proton conductivity of the membranes was measured by the AC impedance technique at controlled temperatures of 30-80 ℃ and R.H. of 50-95%. The conductivity increased as temperature and R.H. was raised. When the membranes had graft chains at the same density, the conductivity increased with their *IEC*. At almost the same *IEC*, membranes with more and shorter graft chains showed higher conductivity compared to those with less and longer chains. This result was explained by the connectivity between hydrophilic domains as proton conducting pathways.

## REFERENCES

[1] T. Okada, H. Satou, M. Okuno, and M. Yuasa, J. Phys. Chem. B, 106, 1267 (2002).

[2] M. Ise, K. D. Kreuer, and J. Maier, Solid State Ionics, 125, 213 (1999).

[3] T. A. Zawodzinsky, J. Davey, J. Valerio, and S. Gottesfeld, Electrochimi. Acta, 40, 297 (1995).

[4] T. D. Gierke, G. E. Munn, and F. C. Wilson, J. Polym. Sci. Polym. Phys. Ed., 19, 1687 (1981).

[5] K. D. Kreuer, J. Membr. Sci., 185, 29 (2001).

[6] T. Yamaki, M. Asano, Y. Maekawa, Y. Morita, T. Suwa, J. Chen, N. Tsubokawa, K. Kobayashi, H. Kubota, and M. Yoshida, Radiat. Phys. Chem., 67, 403 (2003).

[7] T. Yamaki, K. Kobayashi, M. Asano, H. Kubota, and M. Yoshida, Polymer, 45, 6569 (2004).

[8] P. D. Beattie, F. P. Orfino, V. I. Basura, K. Zychowska, J. Ding, C. Chuy, J. Schmeisser, and S. Holdcroft, J. Electroanal. Chem., 503, 45 (2001).

(Received December 23, 2004; Accepted September 26, 2005)