

EFFECT OF PRE- γ -IRRADIATION DOSE ON THE DURABILITY OF THE SULFONATED ETFE-G-POLYSTYRENE CONDUCTING MEMBRANES

Upita Septiani¹ and Hitoshi Kubota²

¹Departement of Chemistry, Faculty of Mathematics and Natural Sciences,
Andalas University

²Department Of Chemistry, Graduate School Of Engineering, Gunma University, Japan

¹Email : upitas@yahoo.com

ABSTRACT

The influence of pre- γ -irradiation dose on durability of the poly(ethylene-co-tetrafluoroethylene) (ETFE) film-based radiation-grafted polymer electrolyte membrane was investigated. The durability of membrane was found to be strongly influence by γ -ray pre-irradiation dose. The durability was tested in a 3% H₂O₂ aqueous solution at 60 °C. The durability of the polymer electrolyte membrane with a degree of grafting of about 30% prepared by lower pre-irradiation dose was more stable than that of the membrane prepared with higher pre-irradiation dose.

Keywords : *Polymer electrolyte membrane, irradiation dose, durability*

INTRODUCTION

Radiation grafting is a well-established technique for the preparation of polymer electrolyte membranes for fuel cells. A great deal of work has been dedicated to preparing various fuel cell membranes using the radiation grafting method. The nature of the base films is an important parameter, which is in close relation to the properties of the fuel cell membranes. The partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE) films combined with hydrocarbon and fluorocarbon structures have a higher radiation resistance and better mechanical property. The former makes it possible to be highly γ -ray pre-irradiated for subsequent grafting, and the latter makes possible to be tolerated in a fuel cell stack for a long time^[1-5].

Because of the long-term durability of polymer electrolyte membrane, the fluoropolymer films are often chosen as the base films^[5-8]. Poly(ethylene-co-tetrafluoroethylene) (ETFE) films are partially fluorinated materials, in which the hydrocarbon ethane units and the fluorocarbon tetrafluoroethylene units are contained. The ETFE films have been the subjects of many studies on development of

the polymer electrolyte fuel cell membrane because of its high performance in thermal and chemical stability, radiation resistance and mechanical properties^[9-11]. The high radiation resistance makes it can be applied in γ -rays pre-irradiation for subsequent grafting, and the high thermal and chemical properties make the resultant membrane possible to be tolerated in a fuel cell for a long time^[10]. In our previous study, it has been reported that the preparation and properties of the the Sulfonated ETFE-g-polystyrene conducting membranes was considerably influenced by the pre-irradiation dose and the grafting time. The similar degree of grafting of about 30 % could be obtained in a short grafting time when a high pre-irradiation dose carried out. The high pre-irradiation dose increases the number of graft chains. On the other hand, the degree of grafting of about 30% can be prepared in a long grafting time when a low pre-irradiation dose was carried out. In the case of longer grafting time, the longer graft chains can be obtained^[12-14]. In this work, we studied the effect of graft conditions, particularly radiation dose and grafting time on the durability of the sulfonated polystyrene-grafted ETFE polymer electrolyte membranes for fuel cells.

EXPERIMENTAL

Materials

180 \times 50 μm thick poly(ethylene-co- α -fluoroethylene) (ETFE) films (Asahi Glass Co. Ltd, Japan) were used as the base films for the preparation of polymer electrolyte membrane. The monomer of styrene (purity > 99%) was purchased from Wako Pure Chemical Ind., Ltd., Japan and use without any further purification. The chlorosulfonic acid, 1,2-dichloroethane, H_2O_2 and toluene were obtained from Wako Pure Chemical Ind., Ltd, and used as received.

Membrane preparation

The process for the preparation of the polymer electrolyte membranes involves three steps. As the first step, a glass tube which was filled ETFE films in the size of 2 cm x 3 cm was degassed for 12 h, and argon gas was then filled in the tube for the γ -ray pre-irradiation at room temperature. The γ -ray irradiation was carried out using a ^{60}Co source facility of Japan Atomic Energy Agency (JAEA). The pre-irradiation dose was 5, 10, 15, 30, 45 and 60 kGy (1 Gy = 1 J g^{-1} energy absorbed). For the 5 and 10 kGy irradiation doses, the dose rates were 5 and 10 kGy/h, respectively. For the other irradiation doses, the dose rate was fixed at 15 kGy/h. After the pre-irradiation, an argon gas-bubbled 40 vol % solution of styrene in toluene was immediately added to the tube. The grafting reactions were performed at 60 $^\circ\text{C}$ in a thermostatic bath for different duration of grafting time (0 ~ 5 h). After reaction, the films were taken out from the tube and extracted by toluene to remove the excess of styrene monomer and the formed homopolymer. The grafted films obtained were then dried under vacuum oven at 40 $^\circ\text{C}$ for 3 h to get the constant weight. The degree of grafting is the percent increased in weight of the ETFE films after the grafting and was calculated as $(W_g - W_0)/W_0 \times 100$, where W_g and W_0 are the weights of grafted and original films, respectively. The grafted films were sulfonated in a 0.2 M solution of chlorosulfonic acid in 1,2-dichloroethane at 60 $^\circ\text{C}$ for 8 h, hydrolyzed in distilled water at 80 $^\circ\text{C}$ for 12 h. Thus, the polymer electrolyte membranes were obtained.

Membrane durability

The chemical stability was characterized by the weight loss of the membrane in a H_2O_2 aqueous solution. The membrane with a size of 2 cm \times 2 cm was immersed in the 3% H_2O_2 aqueous solution at 60 $^\circ\text{C}$. During the immersion, the membrane was intermittently taken out of the solution and weighed after wiping off the excess surface water. The percent of weight residue of the membrane was calculated:

$$\text{weight}(\%) = \frac{W_{\text{wet}(t(h))}}{W_{\text{wet}(0(h))}} \times 100\%$$

where the $W_{\text{wet}(0(h))}$ is the initial weight of the membrane before test, and the $W_{\text{wet}(t(h))}$ is the weight of the membrane after soaking in 3 % H_2O_2 aqueous solution for the total time of t hours.

FT-IR measurement

Characteristic of membranes degradation was confirmed by means of Fourier transform infrared (FT-IR) spectroscopy. The instrument used was a JASCO FT-IR-5300 Spectrometer (Japan Spectroscopic Co., Ltd.).

RESULTS AND DISCUSSION

Membrane durability

The lifetime of the polymer electrolyte membranes fuel cell is considerably limited by the chemical stability of the membrane. The degradation of the polymer electrolyte membranes is mainly due to the formed hydroxyl radicals in the fuel cell. In the fuel cell operation, the oxygen diffuses through the membrane and incompletely reduces, resulting in the formation of H_2O_2 near the anode side. The H_2O_2 can be decomposed under high temperature, forming the hydroxyl radicals, which will attack on the α -hydrogen of graft chains, leading to the severe degradation of the membrane. Testing polymer electrolyte membrane lifetime in actual fuel cells is time-consuming and expensive. Therefore, in this study, the long-term durability of membranes obtained was evaluated in a 3% H_2O_2 aqueous

solution at 60 °C. The weight of membrane in H₂O₂ solution was determined as a function of time.

Fig. 1 shows the durability time measurement of sulfonated ETFE membrane with degree of grafting of about 30 % and ion exchange capacity of about 1.6 mmol/g. It was found that the membrane prepared with 60 kGy of pre-irradiation dose are initially stable more than 36 h in the 3% H₂O₂ aqueous solution, then the weight of the membrane rapidly decreased due to the decomposition of the polystyrene sulfonic acid chains in the sulfonated ETFE membranes. Finally, the weight of the

membranes became constant, approached the weight of original ETFE films, indicating that the graft chains and sulfonic acids groups have completely left the polymeric base films. In this chapter, the durability time of the polymer electrolyte membranes is defined as the middle point between the time that the decrease in weight of the membrane just occurred and the time that the weight of the membrane became constant again. Therefore, as shown in the figures, the membrane prepared with 60 kGy of pre-irradiation dose has a durability time of 52 h.

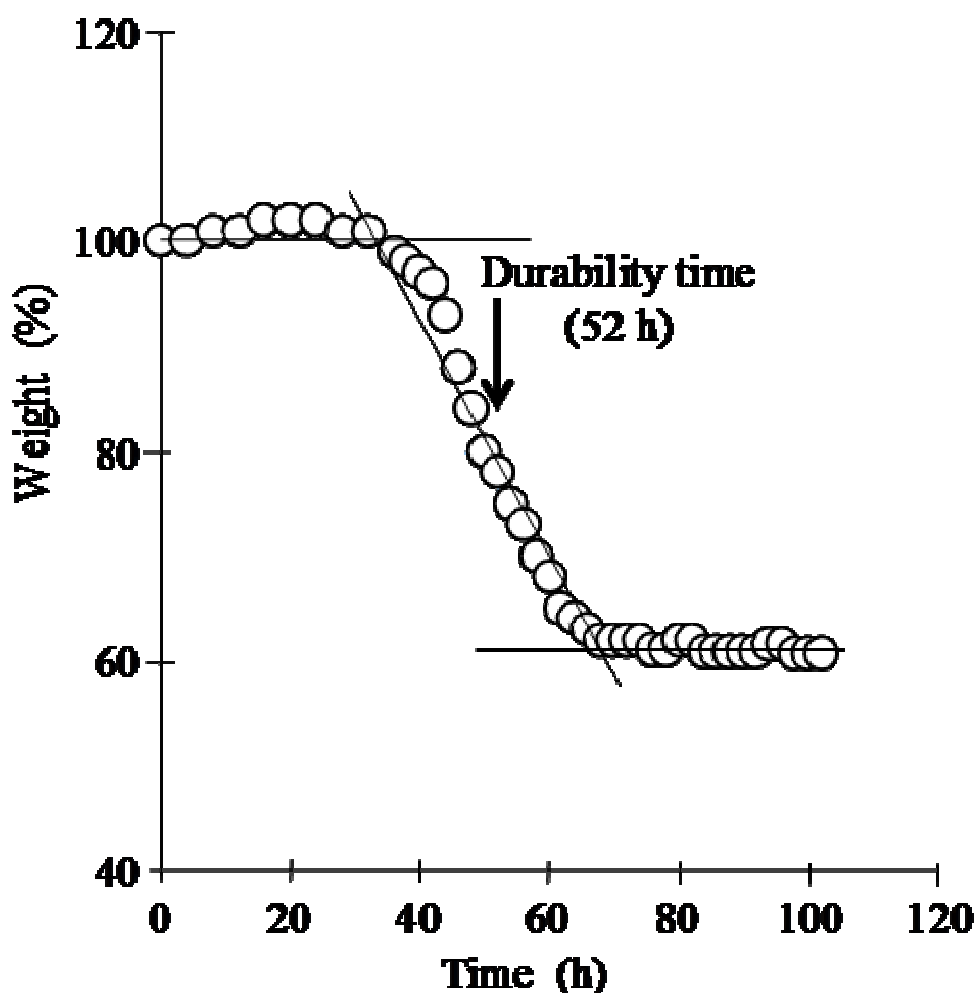


Figure 1. Change in weight of sulfonated ETFE membranes in a 3% H₂O₂ aqueous solution at 60°C. A polymer electrolyte membrane (degree of grafting: 30%; IEC: 1.6 mmol/g) was prepared by post grafting at 60°C after pre- γ -irradiation with a dose of 60 kGy.

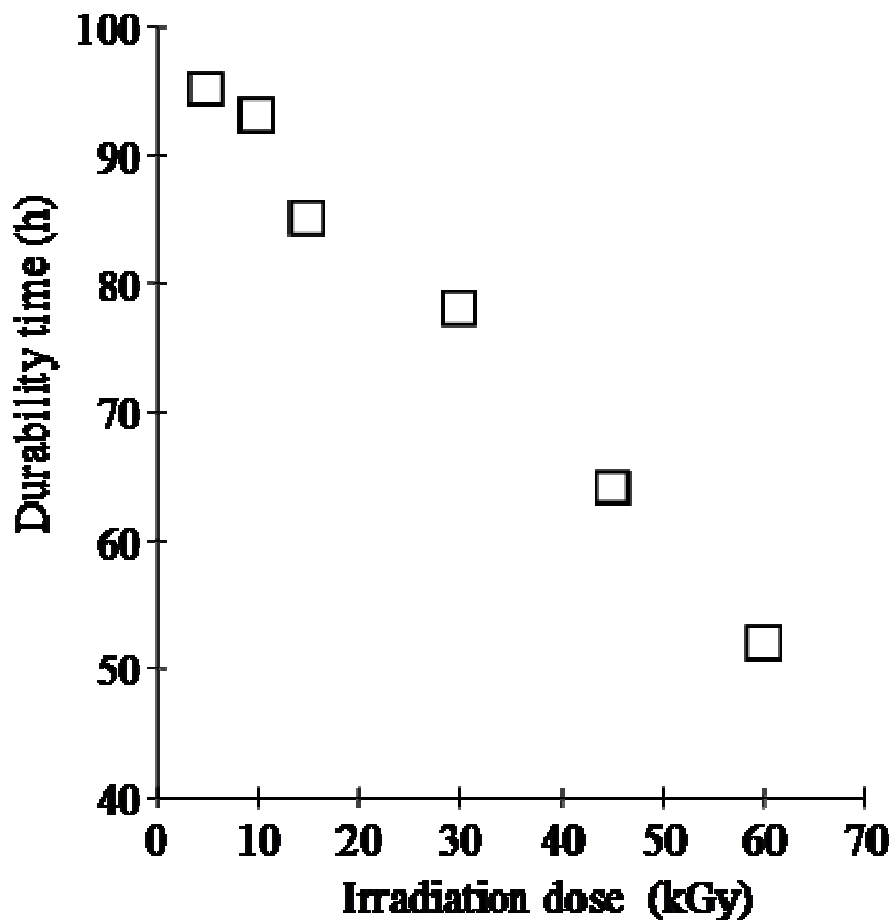


Figure 2. Chemical stability as a function of pre- γ -irradiation dose for sulfonated ETFE membranes (degree of grafting: 30%; IEC: 1.6 mmol/g) in a 3% H_2O_2 aqueous solution at 60°C.

Fig. 2 shows a plot of the durability time of the sulfonated ETFE membranes, with the similar degree of grafting of about 30 % and the similar ion exchange capacity of about 1.6 mmol/g, as a function of pre-irradiation dose. It seems clearly that the sulfonated ETFE membrane prepared with the lowest pre-irradiation dose of 5 kGy gave the longest durability time of about 95 h, this may be attributed to the longest graft chains uniformly distributed in the membrane. The durability time decreases with the increase in the pre-irradiation dose. For the membrane prepared with a high pre-irradiation dose of 60 kGy, the durability time was only about 52 h.

Characteristics of the membrane degradation

The durability of the membranes was evaluated in a 3 % H_2O_2 aqueous solution at 60°C. After

a certain time, the weight of the membranes in the test solution decreased due to the decomposition of the polystyrene sulfonic acid. The degradation was confirmed by FTIR measurement. Fig. 3-3 shows the Fourier transform infrared (FT-IR) spectrum of (a) original ETFE films, (b) grafted ETFE films, which was prepared with 30 kGy of pre-irradiation dose and has a degree of grafting of about 30% (c) sulfonated ETFE-g-PSt, (d) sulfonated ETFE-g-PSt after durability test for 2 h and (e) sulfonated ETFE-g-PSt after durability test for 70 h. As shown in the Figures, the bands in the range $980 - 1250 \text{ cm}^{-1}$ assigned to the ETFE presented on all the curves. However, the new peak of 750 cm^{-1} can be found for the grafted film. After sulfonation, the broad bands at 770, 836 and 1007 cm^{-1} assigned to the symmetric and asymmetric stretches of sulfonic acid groups, were appeared on the spectra of the radiation

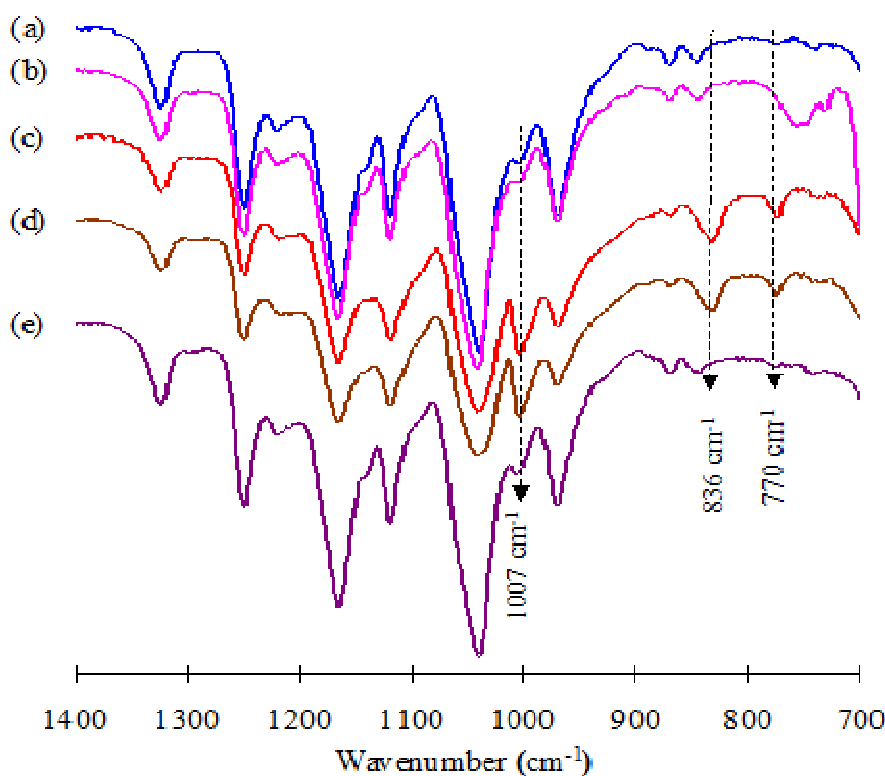


Figure 3. FTIR spectra of (a) ETFE films, (b) grafted ETFE films prepared with 30 kGy of irradiation dose (degree of grafting: 30%), (c) sulfonated ETFE-g-PSt, (d) sulfonated ETFE-g-PSt after durability test for 2 h and (e) sulfonated ETFE-g-PSt after durability test for 70 h.

grafted ETFE electrolyte membrane. Furthermore, the spectrum of the electrolyte membrane with a durability test of 2 h was almost not changed in comparison with the original polymer electrolyte membrane, indicating that the membrane was stable enough to the 2 h durability test. However, with a long durability test of about 70 h, the graft chains and sulfonic acid groups were decomposed completely. Therefore, the spectrum of the 70 h tested membrane showed the very similar spectrum to the original ETFE film. The degradation was due to the scission of the C-C bond of the graft chain, resulting in the graft chain together with the sulfonic acid group leaving the ETFE base films.

CONCLUSION

The sulfonated ETFE-g-polystyrene conducting membranes have been prepared by pre- γ -irradiation grafting of styrene into ETFE followed by sulfonation of the grafted films. The durability of the membranes was evaluated

in a 3 % H_2O_2 aqueous solution at 60°C. It was concluded that the polymer electrolyte membrane with a degree of grafting of about 30 % prepared by lower pre-irradiation dose was more stable than that of the membrane prepared with higher pre-irradiation dose.

REFERENCES

1. M. M. Nasef, H. Saidi, A. M. Dessouki, and E. M. El-Nesr, *Polym Int.*, 49, 399 (2000).
2. F. N. Büchi, B. Gupta, O. Haas, and G. G. Scherer, *Electrochimica Acta*, 40, 345 (1995).
3. B. Gupta, and G.G Scherer, *Chimia*, 48, 127 (1994).
4. V. Y. Karbanov, R. E. Aliev, and V. N. Kudryavtsev, *Radiat. Phys. Chem.*, 37, 175 (1991).
5. J. Chen, M. Asano, T. Yamaki, and M. Yoshida, *J. Membr. Sci.*, 269, 194 (2006).

6. T. Momose, H. Yoshioka, and I. Ishigaki, *J. Appl. Polym. Sci.*, 37, 2817 (1989).
7. S. Holmberg, J. H. Näsman, and F. Sundholm, *Polym. Adv. Technol.*, 9, 121 (1998).
8. A. S. Aricò, V. Baglio, P. Cretì, A. D. Blasi, V. Antonucci, J. Brunea, A. Chapotot, A. Bozzi, and J. Schoemans, *J. Power Sources*, 123, 107 (2003).
9. B. Mattsson, H. Ericson, L. M. Torell, and F. Sundholm, *Electrochimica Acta*, 45, 1405 (2000).
10. J. A. Horsfall, and K. V. Lovell, *Polym. Adv. Technol.*, 13, 381 (2002).
11. M. M. Nasef, H. Saidi, and K. Z. M. Dahlan, *Radiat. Phys. Chem.*, 68, 875 (2003).
12. U. Septiani, J. Chen, M. Asano, Y. Maekawa, M. Yoshida, and H. Kubota, *J. Mater. Sci.*, 42, 1330 (2007).
13. J. Chen, U. Septiani, M. Asano, Y. Maekawa, M. Yoshida, and H. Kubota, *J. Appl. Polym. Sci.*, 103, 1966 (2007).
14. U. Septiani, *Prosiding Seminar Nasional Kimia dan Pendidikan Kimia*, ISBN: 978-602-8821-28-5, 74-84 (2011)