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Influence of pre-irradiation atmosphere on the properties of polymer electrolyte membranes prepared using radiation grafting method

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Abstract The influence of pre-irradiation atmosphere, argon and air, on radiation grafting of styrene into poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films and the properties of the ETFE-based radiation-grafted polymer electrolyte membranes were investigated. The preparation and properties of the membranes were found to be strongly influenced by the γ-ray pre-irradiation atmosphere. The proton conductivity was measured in its water-saturated state at 25 °C, and the membrane durability was tested in a 3% H_2O_2 aqueous solution at 60 °C. The proton conductivity of the membrane prepared by pre-irradiation under air was higher than that of the membrane prepared under argon with the same ion exchange capacity level. However, the durability of the former was considerably lower than that of the latter. For instance, the membrane with an ion exchange capacity of about 1.0 mmol g^{-1} prepared under argon was twice as durable as that prepared under air. It was considered that the lower durability of the membrane prepared by pre-irradiation under air was because of the unstable ether bond introduced between the graft chains and the backbone chains.

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Introduction

Radiation grafting is a well-established technique for the preparation of polymer electrolyte membranes for fuel cells. The advantages of the radiation grafting method include the lack of need for chemical initiators, the easy preparation from the already preformed films, and the easy control of the proton conductivity [1–4]. 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. Both hydrocarbon and fluorocarbon films have been used as base films for the fuel cell membrane preparation [1–4]. Basically, the base films have to meet certain requirements, such as the easy generation of stable free radicals upon exposure to high-energy radiation and high resistance towards radiolytic degradation. The partially fluorinated poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films combined with hydrocarbon and fluorocarbon structures have a higher radiation resistance and a better mechanical property. The former makes it possible to be highly γ-ray pre-irradiated for subsequent grafting [5], and the latter makes possible to be tolerated in a fuel cell stack for a long time [6].

Therefore, the ETFE films have been the subject of many studies related to polymer electrolyte fuel cell membrane development [7–9]. Recently, various correlations between the properties of ETFE-based membranes and their respective fuel cell performances have been reported [9]. Styrene is the most common monomer for grafting. Radiation grafting can be carried out using the simultaneous (direct or mutual) irradiation method or the pre-irradiation grafting (post-grafting) method [3, 4]. The simultaneous irradiation method is a simple technique for preparation of graft materials. However, it has a serious limitation arising from the high level of homopolymer formation. In contrast, the pre-irradiation method has been given much attention because there is little homopolymer formation and grafting can be carried out at any time, away from radiation sources [10]. The pre-irradiation grafting method for the preparation of polymer electrolyte membranes involves three steps: pre-irradiation of the base film by exposure to γ-rays or electron-beams, grafting in a monomer solution under an oxygen-free atmosphere, and finally sulfonation. Pre-irradiation is usually carried out under air or an oxygen-free atmosphere at room temperature. The behavior of polymer films in radiation environments and the effect on the properties of the resulting membrane are of considerable interest for the development of commercial fuel cell membranes. In practice, pre-irradiation under air is more suitable for industrial fabrication. In this study, the effect of the pre-irradiation atmosphere on the preparation and properties of polymer electrolyte membranes were investigated and discussed.

Experimental part

Fifty micrometer thick poly(ethylene-*co*-tetrafluoroethylene) (ETFE) films supplied by Asahi Glass Co. Ltd were used as the base films for the preparation of polymer electrolyte membranes. This was done by radiation grafting of styrene into the ETFE films using the pre-irradiation method and subsequent sulfonation. Argon and air were used as the pre-irradiation atmosphere for the preparation of the membranes.

For the pre-irradiation under argon, a glass tube with added ETFE films in the size of 20 mm × 30 mm was degassed for 12 h, and argon gas was then filled in the tube for the γ-ray pre-irradiation at room temperature with a dose of 10 kGy (1 Gy = 1 J g^{-1} energy absorbed). The dose rate was 10 kGy/h. The radiation source (Japan Atomic Energy Agency) is originated from Co-60 source, which has a capacity of 1.22×10^{16} Bq (3.29×10^{6} Ci). After the pre-irradiation, argon gas-bubbled 40 vol% styrene monomer of toluene solution was quickly added to the tube. The grafting reaction was initiated by placing the tube in a thermostatic bath controlled at 60 °C.

On the other hand, for the pre-irradiation under air, the ETFE films in the size of 20 mm × 30 mm were γ-ray pre-irradiated under air at room temperature with a dose of 10 kGy. The pre-irradiated films together with 40 ml of styrene and 60 ml of toluene were added into a flask and then deaerated by argon bubbling. After 30 min, the grafting system was heated to 60 °C to initiate the graft polymerization. During the grafting, the monomer solution was continuously deaerated by argon bubbling.

After the grafting, the grafted films were extracted with toluene to remove the ungrafted polymer and residual monomers, and dried in a vacuum oven at 60 °C for 12 h. The degree of grafting was calculated as $(W_g–W_0)/W_0 \times 100$, where W_0 and W_g are the film weights before and after the grafting, respectively. The grafted films were sulfonated in a 0.2 M chlorosulfonic acid solution of 1,2-dichloroethane at 60 °C for 8 h in a sealed bottle, hydrolyzed in distilled water at 80 °C for 12 h. Thus, the polymer electrolyte membranes were obtained.

The ion exchange capacity of the obtained polymer electrolyte membrane was determined by acid–base titration using an automatic titrator (HIRANUMA COM-555). The dried membrane in the protonic form (about 80 mg) was immersed in 20 ml of NaCl saturated aqueous solution and equilibrated for 24 h. The solution was then titrated with 0.1 M NaOH solution. Based on the titration results, the ion exchange capacity was calculated as $0.1V_{\mathrm{NaOH}}/W_{\mathrm{dry}}$, where V_{NaOH} (ml) is the volume of the 0.1 M NaOH solution at pH 7.0, and W_{dry} (g) is the dry weight of the membrane in the protonic form. The theoretical ion exchange capacity was calculated as $1000d/(100M_1+dM_2)$, where d is the degree of grafting, M_1 and M_2 are 104 and 184, being the molecular weights of styrene and styrene sulfonic acid, respectively.

Proton conductivity of the membrane at 25 °C was obtained by impedance spectroscopy measurement using a Solartron 1269 analyzer with an AC perturbation of 10 mV. The samples were hydrated in water overnight before measurement and clamped between two Pt electrodes for recording of the impedance spectroscopy. The real impedance taken at zero imaginary impedance was used to calculate the proton conductivity of the membrane.

The durability of the membrane was characterized by the weight loss of the membrane in a H_2O_2 aqueous solution. The membrane with a size of 20 mm × 20 mm was immersed in the 3% H_2O_2 aqueous solution at 60 °C. During the immersion, the membrane was intermittently taken out of the solution and weighed after wiping off the excess surface water.

Results and discussion

The preparation of an ETFE-based polymer electrolyte membrane involves pre-irradiation, grafting and finally sulfonation. Pre-irradiation of the ETFE films under argon induces the scissions of C–F, C–H and C–C bonds, leading to the formation of polymer radicals, which can initiate the graft polymerization [5]. In the case of pre-irradiation under air, the formed polymer radicals can react with the oxygen, generating hydroperoxides, which are stable at room temperature but can decompose to peroxy radicals at an elevated temperature. Both the polymer radicals and the hydroperoxides can act as active sites for initiating the graft polymerization. Therefore, upon the addition of the pre-irradiated films to the styrene solution at an elevated temperature, graft polymerization occurs. Scheme 1 shows a possible process for the preparation of the membranes with two pre-irradiation atmospheres, argon and air. Obviously, different pre-irradiation atmospheres lead to grafted films with different chemical structures and in turn to final membranes with different properties.

The pre-irradiated ETFE films were reacted with styrene at 60 °C under oxygen-free conditions for different durations. The grafting kinetic curves for the films pre-irradiated under air and argon are shown in Fig. 1. The degree of grafting, which indicates the total

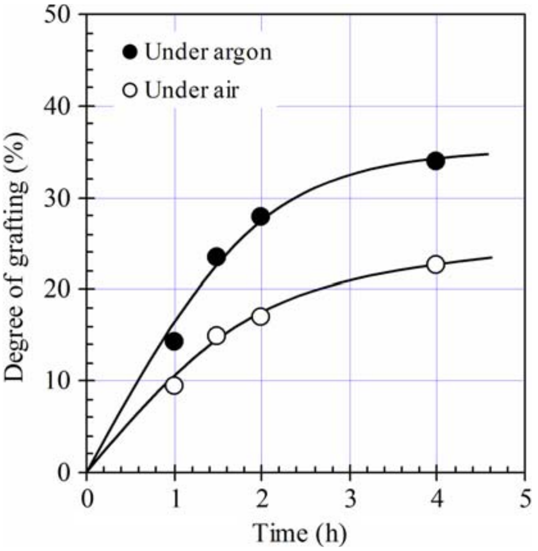
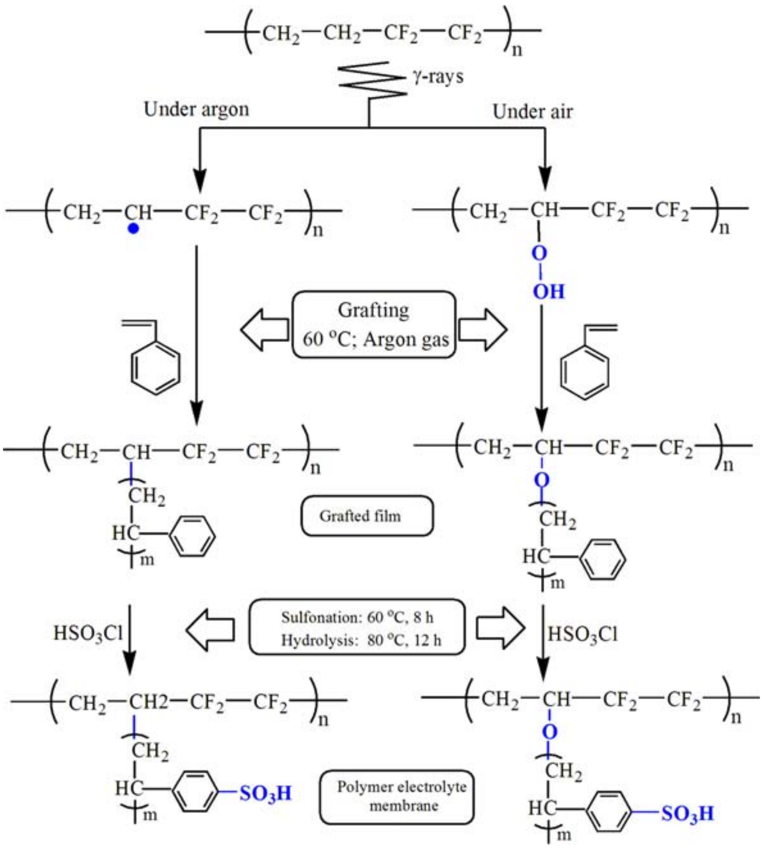


Fig. 1 Graft kinetics of the ETFE films pre-irradiated under argon and air. Pre-irradiation dose, 10 kGy; grafting temperature, 60 °C

Scheme 1 Process for the polymer electrolyte membrane preparations from the ETFE films pre-irradiated under argon and air



weight percent of the graft chains attached into the base films, linearly increases in the first 2 h and then deviates from the linear behavior. Clearly, the degree of grafting is strongly influenced by the pre-irradiation atmosphere, as it is higher under argon than under air over the entire grafting time region. This is because of the higher activity of the polymer radicals formed under an argon pre-irradiation atmosphere than that of the hydroperoxides formed under an air pre-irradiation atmosphere. In addition, the polymer radicals can directly initiate the graft polymerization, whereas the hydroperoxides have to decompose to peroxy radicals at elevated temperatures before initiating the grafting reaction. The grafting rate of the film pre-irradiated under air is not only controlled by the monomer diffusion but also by the decomposition of the hydroperoxides. Therefore, the grafting ability of the films pre-irradiated under air is considerably lower. For instance, as shown in Fig. 1, the degree of grafting at 4 h is 33.9% for the film pre-irradiated under argon and is only 22.6% for the film pre-irradiated under air; the former is almost 50% higher than the latter.

The grafted ETFE films were sulfonated in order to obtain the polymer electrolyte membranes. Sulfonation is a powerful and versatile process, which can be used to simultaneously render the polymers proton conductive as well as hydrophilic in nature. Chlorosulfonic acid was chosen as a sulfonating agent as it is highly reactive in electrophilic substitutions of aromatic rings and convenient for laboratory study [11]. Suitable solvent was 1,2-dichloroethane as it is a good solvent for chlorosulfonic acid. At the condition of the excess of chlorosulfonic acid, the formation of sulfonyl chloride groups (–SO_2Cl) is more pronounced [12]. The –SO_2Cl on the aromatic rings is considerably stable in pure water at room temperature. For instance, the electric resistance was almost not changed for the sulfonated membrane treated in the water at room temperature even for 3 days; while in the water at 80 °C, it drastically decreased by several orders of magnitudes after 4 h. In this study, we carried out the hydrolysis in distilled water at 80 °C for 12 h. The resulted material appears to be a tough, transparent and flexible membrane at its water-saturated state. The introduction of –SO_3H into the grafted films creates a two-phase structure: hydrophobic and hydrophilic. The ion exchange and proton conductivity are due to the hydrophilic phase in the membranes.

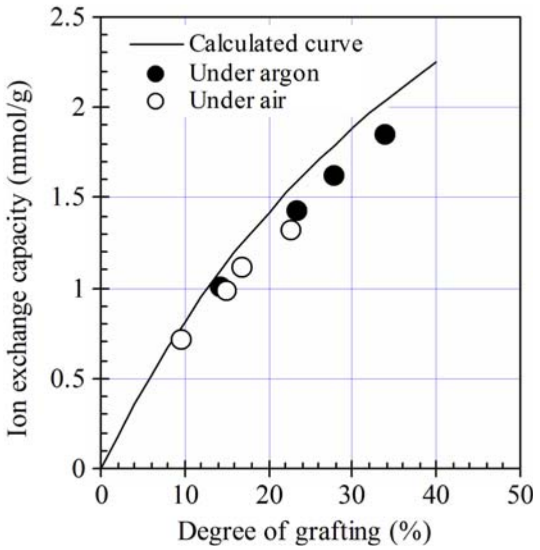


Fig. 2 Ion exchange capacities of the polymer electrolyte membranes prepared by pre-irradiation under argon and air

The ion exchange capacities of the prepared polymer electrolyte membranes were determined by acid–base titration. As shown in Fig. 2, the ion exchange capacity increases with the increasing degree of grafting, and is independent of the pre-irradiation atmosphere. The membrane prepared with an argon pre-irradiation atmosphere reaches a higher maximum ion exchange capacity of 1.86 mmol g^{-1}, whereas the membrane prepared with an air pre-irradiation atmosphere displays a relatively lower maximum ion exchange capacity of 1.32 mmol g^{-1}. The theoretical curve of the ion exchange capacity is a function of the degree of grafting and is given in Fig. 2. The detected ion exchange capacities are all distributed near the theoretical curve, indicating the degree of sulfonation to be about 90%. Therefore, the ion exchange capacity could be freely controlled by changing the degree of grafting.

The Proton conductivity and durability are the basic requirements of fuel cell membranes. The proton conductivity depends on the number of available acid groups (ion exchange capacity) and the dissociation capability in water. In this study, the proton conductivity was measured in the water-saturated state at 25 °C. Figure 3 shows the proton conductivity as a function of degree of grafting of the membranes prepared by pre-irradiation under air and argon. The proton conductivity linearly increases with the increasing degree of grafting, and is quite dependent on the pre-irradiation atmosphere. For instance, with a degree of grafting of about 23%, the proton conductivity is 0.051 and 0.032 S cm^{-1} for the membranes prepared by pre-irradiation under air and argon, respectively. The membrane prepared by pre-irradiation under air shows a higher proton conductivity than that prepared under argon. This is due to the ether bonds (–O–) introduced between the graft chains and the backbone chains of

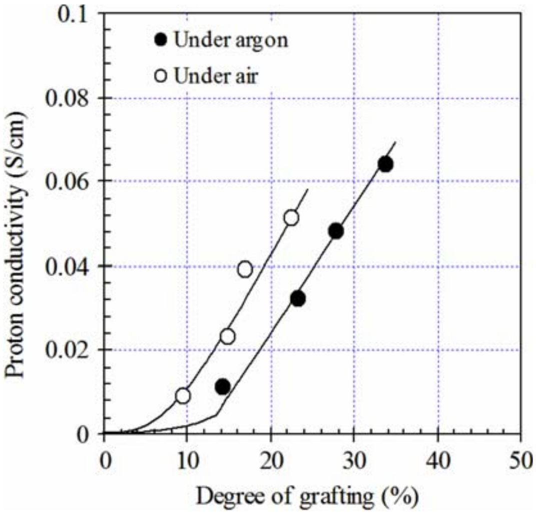


Fig. 3 Proton conductivity of the polymer electrolyte membranes prepared by pre-irradiation under argon and air

the membrane prepared by pre-irradiation under air. The ether bonds increase the membrane hydrophilicity, resulting in the higher water uptake, consequently, a higher proton conductivity of the membrane.

The membrane degradation in a fuel cell is mainly because of the H_2O_2 originating from the incomplete reduction of the oxygen [13]. However, testing the durability of a new membrane in actual fuel cells is both time-consuming and expensive. Therefore, the membrane durability was tested in a 3% H_2O_2 aqueous solution at 60 °C. The weight of the membrane in the H_2O_2 solution was determined as a function of time. Figure 4 shows the weight changes of the two membranes prepared by pre-irradiation under argon and air, respectively, with a similar ion exchange capacity of about 1.0 mmol g^{-1}. Both membranes are initially stable in the 3% H_2O_2 solution for more than 30 h, then decomposition occurs. The decomposition in the H_2O_2 solution is caused by the HO· radical attack on the α-hydrogen of the graft chains [13]. As shown in Fig. 4, the decompositions occur after 30 h with the membrane prepared by pre-irradiation under air, but after 60 h with the membrane prepared by pre-irradiation under argon. Therefore, the membrane prepared by pre-irradiation under argon is twice as durable as the membrane prepared by pre-irradiation under air. After the degradation, the properties of the residue films, such as the appearance, thickness and Fourier transform infrared (FT-IR) spectra, are very similar to that of the original ETFE film [14]. We concluded that the weight loss of the polymer electrolyte membrane in the H_2O_2 solution was due to the scission of the C–C bonds of the graft chains, resulting in the graft chains together with the sulfonic acid groups leaving the ETFE base films. This was different from the thermal decomposition in the thermogravimetric (TG) analysis, where the decomposition of the sulfonic acid groups was first occurred due to the scission of the S–C bonds between the sulfonic acid groups and the aromatic rings [14].

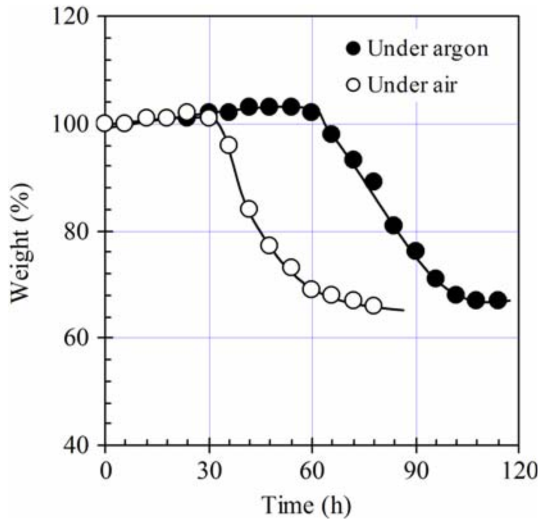


Fig. 4 Membrane durability of the polymer electrolyte membranes prepared by pre-irradiation under argon and air. Ion exchange capacity, 1.0 mmol g^{-1}; test condition, in 3% H_2O_2 solution at 60 °C

Figure 5 shows the effect of ion exchange capacity on the durability time of the radiation-grafted membrane prepared by pre-irradiation under argon and air. Obviously, the durability time linearly decreases with the increasing ion exchange capacity of the membrane.

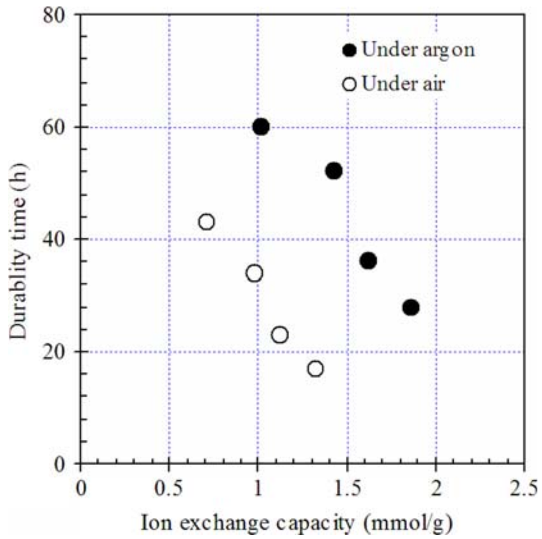


Fig. 5 Effect of ion exchange capacity of the polymer electrolyte membrane on the membrane durability. Test condition, in 3% H_2O_2 solution at 60 °C

The shorter durability time of the membrane with higher ion exchange capacity was due to its higher hydrophilicity, which is more favorable for the $HO^{\bullet}$ radicals diffusion into it. In addition, the membrane durability was found to be strongly affected by the pre-irradiation atmosphere of the films; the membrane prepared by pre-irradiation under argon shows considerably longer durability time than that prepared under air in the entire ion exchange capacity region. This is due to the unstable ether bonds introduced between the graft chains and the backbone chains of the membrane prepared by pre-irradiation under air. The enhanced hydrophilicity by the ether bonds is another possible reason for the relevant shorter durability time of the membrane. In view of this point, pre-irradiation under oxygen-free atmosphere was recommended for the preparation of the crosslinked radiation-grafted polymer electrolyte membranes.

Conclusions

The ETFE films were successfully grafted with styrene after they were pre-irradiated under argon or air. It was found that the grafting ability is strongly influenced by the pre-irradiation atmosphere, as the degree of grafting is considerably higher under argon than under air in the entire grafting time region. The sulfonation of the grafted ETFE films can reach a higher extent about 90% and is independent of the pre-irradiation atmosphere. The proton conductivity of the membrane prepared by pre-irradiation under air is higher than that of the membrane prepared under argon. The durability of the membrane was tested in a 3% H_2O_2 aqueous solution at 60 °C. The durability time of the membrane linearly decrease with the increase in degree of grafting, and it is considerably shorter for the membrane prepared under air than under argon in the entire degree of grafting region. Especially, at a similar ion exchange capacity of about 1.0 mmol g^{-1}, the durability time of the membrane prepared by pre-irradiating under argon is twice as durable as that prepared under air. The shorter durability time of the membrane prepared by pre-irradiation under air was because of the unstable ether bond introduced between the grafted chains and the backbone chains.

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