

Manufacture of ETFE fuel cell membrane by using radiation grafting method

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ABSTRACT: The electron beam radiation technology could be successfully carried out for a manufacture of ETFE (Poly(ethylene-alt-tetrafluoroethylene) membrane with a uniform and high distribution of sulfonic groups. The maximum degree of styrene-grafting existed at around 20kGy, considerably decreasing the degree of grafting above 30kGy. The hydrated ETFE film with a high degree of grafting after sulfonation could be largely swelled, showing a high transparency in water. The methanol crossover across ETFE membrane could be much more suppressed compared to Nafion 115 membrane. On the other hand, electric power generation over ETFE membrane was slightly lower than that in Nafion 115.

Keywords: DMFC, ETFE, electron beam, grafting, styrene, MeOH crossover, IEC, electric power density

1. INTRODUCTION

One of important parts in polymer electrolyte membrane fuel cell (PEMFC) is membrane, which performance is dependent of proton transfer ability from anode to cathode. The polymer membranes can be classified by two classes according to their manufacturing process, i.e. synthesis by the copolymerization, and radiation grafting of monomer onto fluoropolymer film. Both modified films should contain the sulfonic groups in polymeric structure to possess the proton transfer ability.

The representative membrane prepared by copolymerization is Nafion one, which has been manufactured in DuPont Co. [1-2]. Nafion membranes have some disadvantages such as their high cost, low operating temperature and high methanol permeability when used in DMFCs [3].

In the near future, in order to successfully commercialize PEMFCs, a low-cost of membranes should be manufactured. One possible method may be radiation grafting technology, which is capable of grafting of styrene derivatives onto polymer film and subsequently attachment of sulfonic acid groups onto polymer chains through a sulfonation. Fluorinated polymers have been widely used as a base polymer film because of their good chemical and thermal resistances and especially due to its sensitivity to radiation, which can lead to a high degree of grafting. Several kinds of fluorinated polymers such as FEP [4, 12, 13], PTFE [5], and ETFE [6] have been tested as basic film.

The accelerated electron beam presents a good energy sources for grafting effectuation, due to a controllability of absorbed doses as well as a high penetration depth

into polymer film. The accelerated electron beam can be irradiated by two methods: preirradiation and simultaneous irradiation. Both irradiation methods should ensure the homogeneous grafting of monomers inside of film as well as its surface to present a high performance of fuel cell.

This paper modified ETFE film by grafting styrene monomer with simultaneous irradiation method and tested its properties as a fuel cell membrane.

2. EXPERIMENTAL

2.1 Materials

ETFE film with thicknesses of 100 μ m was purchased from Dupont Co. and was used as a base polymer for the manufacturing of PEM. Styrene monomer of reagent grade (Aldrich Co.) was used without further purification. Chlorosulfonic acid and dichloromethane used for sulfonation were of reagent grade (Kanto Chemical) and were also used without further purification. Methanol for the crossover test was of reagent grade (Aldrich Co.).

2.2 Grafting of styrene monomer

The ETFE film with dimensions of 30 x 50mm was grafted by styrene monomer under simultaneous irradiation of electron beam, which was generated from an accelerator with a maximum beam energy of 0.7 MeV and maximum beam current of 35mA (ELV-0.5, BINP in Russia). After irradiating the electron beam onto the ETFE film immersed into styrene monomer, the grafting was performed in a dry oven at controlled temperature. To remove possible homo-polymers in the film, the grafted FEP film was boiled in toluene solution for two hours, followed by washing several times in cold toluene, and it was dried at 80°C for eight hours.

The degree of grafting was estimated by measuring the difference in weight before and after grafting with the following equation:

$$\text{The degree of grafting} = \frac{W_g - W_o}{W_o} \times 100$$

where, W_g and W_o are the weights of the grafted film and the virgin film, respectively.

2.3 Sulfonation of styrene-grafted ETFE

To impart conductivity of the protons to the ETFE film grafted by styrene, the grafted film was sulfonated by boiling it with 0.2M chlorosulfonic acid diluted with dichloro-methane at 60°C for eight hours. After sulfonation, the film was hydrated in deionized water at 80°C for 12hours.

The ion exchange capacity (IEC) [7] was measured using the following procedure: First, the sulfonated ETFE membrane is immersed in a saturated NaCl solution and equilibrated for one day to exchange the H^+ ions in the sulfonic acid groups with Na^+ ions. The equilibrated solution is titrated using 0.1N NaOH solution with an acid-alkaline neutral titration, wherefrom the IEC of the ETFE membrane can be estimated by the following equation.

$$IEC(\text{mmol/g}) = \frac{0.1 \times V_{\text{NaOH}}}{W_d}$$

where V_{NaOH} is the volume of NaOH solution consumed by titration and W_d is the dry weight of the sulfonated ETFE membrane.

The sulfur profile across the sulfonated ETFE film was determined by energy dispersive X-ray analysis using a scanning electron microscope (SAM, S-4200, Hitachi). The film was cut transversely by a razor blade, and the cut section was positioned using epoxy resin and coated by Pt-sputtering. The sulfur contents were measured at seven points across the cross-section of the film, including both the surfaces and center. The sulfur content in the film is the relative weight percentage on the basis of the F, C and S atoms.

2.4 Measurement of methanol crossover

The methanol crossover in the sulfonated ETFE membrane was evaluated by measuring the amounts of methanol

transferred toward opposite side across the ETFE film. Two glass bottles each with a volume of 200 ml were filled with a determined concentration of methanol and distilled water, respectively, and the ETFE membrane was positioned at the joint between the two bottles. The methanol concentration transferred through ETFE membrane on the pure water side was measured by a gas chromatograph (GC-9A, Shimadzu Co.) with an FID detector. The column was packed with Porapak Q (80-100 mesh, Waters Co.) and operated at 120°C under H₂ carrier gas.

3. RESULTS and DISCUSSION

3.1 Grafting of styrene onto ETFE film

Figure 1 shows that the degree of styrene-grafting onto ETFE is strongly affected by irradiation dose: around 20kGy of dose is likely to give a maximum degree of grafting followed by 10kGy, and above 30kGy the degree of grafting was considerably lowered as doses increased. At 100kGy, even five hours of grafting could give only 8.8% of grafting degree and the grafting was unlikely to be increased further. On the other hand, at 10kGy and 20kGy of doses the grafting degree tended to continually increased without its saturation after five hours. High dose of electron beam encourage many several kinds of radicals to be produced onto the polymer chains, but the produced radicals cannot be continually increased with increasing dose and are likely to be limited at a high dose over. Moreover, a too high dose can induce a chain-scission in polymer structure, which might results in a decrease of grafting degree.

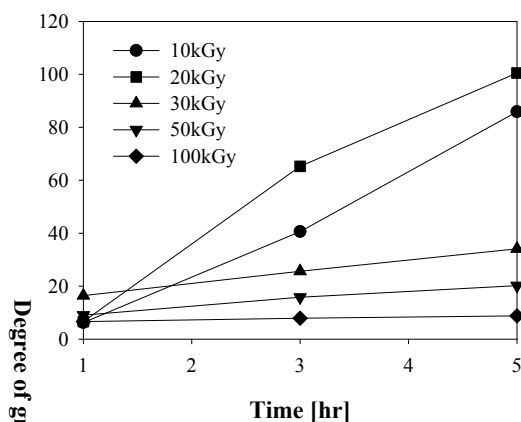


Figure 1: Degree of grafting in ETFE film according to grafting time at several doses with 45°C of grafting temperature.

3.2 Sulfonation of styrene-grafted ETFE film

Since the sulfonic acid group (SO₃H) attached to the styrene molecules is dissociated into SO₃⁻ and H⁺ in aqueous solution, the IEC has a direct relation to the degree of sulfonation. Figure 2 shows that the IEC value increases with increasing degree of grafting. The IEC value of the commercialized Nafion 117 is 0.9mmol/g, which is much lower than that of the ETFE membrane manufactured in this study. The IEC of the ETFE membrane with a degree of grafting of around 50% is equal to that of Nafion 117.

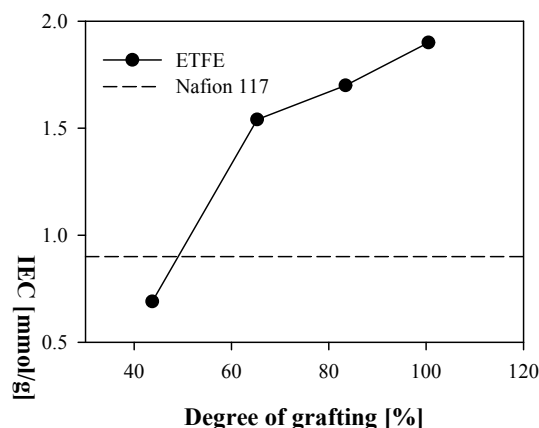


Figure 2: IEC versus degree of grafting at 20kGy of dose, 45°C of grafting time, and 3hr of grafting time.

The sulfur profiles in the sulfonic acid group across the sulfonated membrane may play an important role in the performance of the fuel cell. Some studies [8] showed the sulphur profiles across the sulfonated membranes. The sulphur profile across the film was measured by energy dispersive X-ray analysis (EDS) using a scanning electron microscope. Figure 3 indicates that the grafting is initiated at both surfaces of the film and then propagates toward the inside of the film. In the ETFE film, the sulfur profile at a degree of grafting of 19.64% is concentrated around the surface and tends to penetrate toward the centre of the film as the grafting time increases (as the degree of grafting increased). In which, sulfonic acid groups could exist around the centre of the film with 68.56% of grafting degree after three hours of grafting at 45°C.

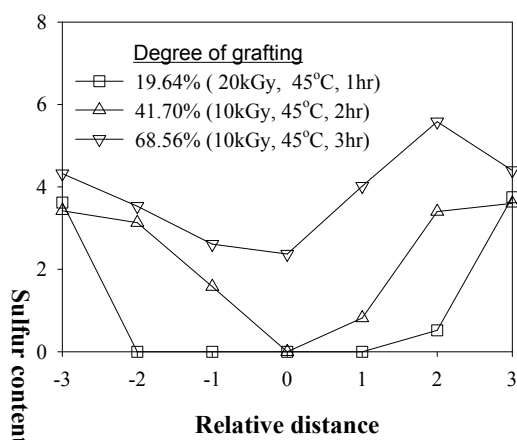


Figure 3: Sulfur profile across the sulfonated ETFE film (100 μ m thickness) at various degrees of grafting.

ETFE film, which was grafted by styrene, was tinged with milky colour, as shown in Photo 1(a). The hydrated ETFE film after sulfonation could be largely swelled and it became transparent in water (Photo 1 (b)), due to a uniform grafting of styrene inside film as well as at the surface. It means that the hydrophobic property of ETFE can be changed to hydrophilic through the sulfonation of the styrene-grafted film, eventually increasing its water-uptake [9].

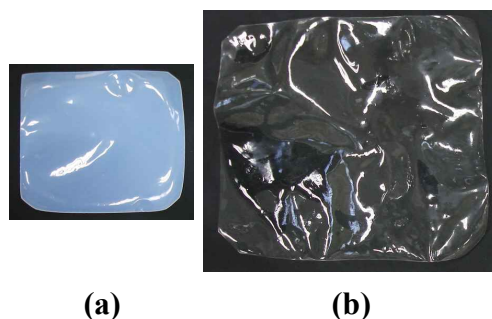


Photo 1: Photographs of grafted ETFE film (100.5%) (a) and hydrated ETFE film (b) after sulfonation (Grafting: 20kGy, 45°C, 5hr).

3.5 Methanol crossover

Methanol at cathode, which was transferred from anode through membrane, causes a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction, resulting in a decrease in the cell performance [10].

Figure 4 shows a crossover in the ETFE membranes at several methanol concentrations of 1wt% to 5wt%. As methanol concentration was higher, the methanol crossover started at earlier time. Comparing ETFE membrane with Nafion 117 membrane, ETFE membrane could much more suppress the methanol crossover.

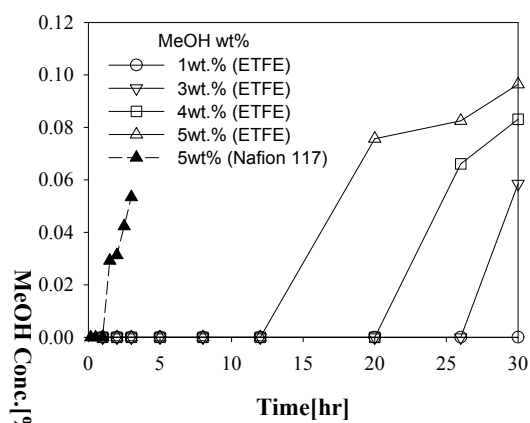


Figure 4: Effects of the MeOH concentration on methanol crossover across ETFE membrane with 57.8% of grafting degree.

3.4 Fuel cell performance

ETFE membranes prepared by radiation technology were tested in the DMFC and compared with Nafion 115 (Table 1). The catalysts on electrodes (anode and cathode) were consisted of 40% of platinum supported by active carbons, which were coated over carbon papers with 1.6mg/cm². Fuel cell was operated at 25°C of cell temperature and 3wt% of MeOH.

ETFE membranes with 50µm and 100µm of thickness generated 1.661mW/cm² and 1.661mW/cm² of electric powers under 5ohm of load, respectively. These values were slightly lower than that in Nafion 115. A 50µm of membrane generated higher electric power due to its lower proton transfer resistance, even though its grafting degree and IEC were low compared to 100µm of membrane.

Table 1: Electric power generation in sulfonated ETFE membrane under 5Ω load in DMFC (concentration of MeOH = 3wt%)

Membranes	ETFE		Nafion 115
Thickness, µm	50	100	125
Grafting, %	66.9	100.3	-
IEC, meq/g	1.54	1.90	0.9
Power density* mW/cm ²	1.834	1.661	1.966

*platinum content on each electrode: 1.6mg/cm², cell temp.: 25°C

4. CONCLUSION

This study adopted the simultaneous irradiation method with an electron beam to manufacture ETFE membrane with a comparably high IEC value. The maximum degree of grafting existed at around 20kGy, and at doses more than 20kGy the degree of grafting was considerably lowered. The grafting of styrene onto the ETFE film was propagated from surface of film into the inner part, eventually spreading uniformly styrene molecules throughout the film. The hydrated ETFE membrane with a high degree of grafting could be largely swelled

after sulfonation and hydration, giving a high transparency in water.

The methanol crossover across ETFE membrane could be much more suppressed compared to Nafion membrane. On the other hand, electric power generation over ETFE membrane was slightly lower than that Nafion 115.

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