

Performance of DMFC with ETFE membrane manufactured by radiation grafting technology

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ABSTRACT: This study manufactured ETFE (Poly(ethylene-alt-tetrafluoroethylene) membrane for DMFC by means of electron beam radiation technology. The maximum degree of styrene-grafting existed at around 20kGy, giving around 100% degree for five hours of grafting at 45°C and 1.9meq/g of IEC (Nafion 115: 0.9meq/g). Electric power of ETFE membrane in DMFC was slightly lower than Nafion 115 membrane, whereas the MeOH crossover in ETFE membrane could be much more suppressed compared to Nafion 115.

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

1. INTRODUCTION

DMFCs (direct methanol fuel cells) or PEMFCs (proton electrolyte membrane fuel cells), which are types of PEFCs (polymer electrolyte fuel cells), can be used for the generation of electric power using a supply of methanol or hydrogen as a fuel, respectively. In recent years, it has been suggested that in the future PEFCs will become one of the most attractive sources of clean energy in automobile, distributed power, and portable power applications [1,2]. Several kinds of fluorinated polymers have been used as the base polymers for manufacturing fuel cell membranes, of which DuPont's Nafion membrane is typically used as the polymer electrolyte membrane (FEM) in PEMFCs, because of its excellent chemical and mechanical stability, as well as its high proton conductivity [3]. However, Nafion membranes have some disadvantages [4] such as their high cost, low operating temperature

and high methanol permeability when used in DMFCs [1,5-7].

Dupont Co. started developing Nafion membranes in 1968 and the most recent version, Nafion 120, has a lifetime of up to 60,000 hours at an operating temperature of 80°C [1]. It has been found that the methanol crossover in a direct methanol fuel cell (DMFC) causes the poisoning of the novel metal catalysts at the cathode [8], resulting in the lowering of the performance of the fuel cell. In the near future, in order to successfully commercialize PEFCs, a low-cost manufacturing method needs to be developed. One possible method may involve the use of radiation technology with an accelerated electron beam for the grafting process in the manufacture of the membrane.

Usually, gamma rays or electron beams can be irradiated by two methods to modify polymers, preirradiation and simultaneous irradiation. Han et al.[9,10] used electron beam radiation technology for the grafting of styrene onto FEP films by means of

simultaneous irradiation under various experimental conditions. In their studies, the styrene molecules could be uniformly grafted to inside as well as surface of ETFE film, giving high values in both IEC and IC.

A solid polymer fuel cell is structured as a set of membrane-electrode assemblies, where each assembly comprises an ion exchange membrane with a catalyst electrode layer formed on both sides of membrane, the membrane is inserted between porous carbon electrodes, and a number of such membrane-electrode assemblies are layered so that a practicable level of power will be supplied. The performance of a fuel cell depends greatly on the catalyst used as the catalyst electrode layer, and a high-performance catalyst is needed not only by solid polymer fuel cells but also by other types of fuel cells.

This study manufactured a fuel cell membrane with ETFE film using radiation-grafting technology and tested electrical characteristics of the membrane in DMFC.

2. EXPERIMENTAL

2.1 Materials

ETFE films with thicknesses of 25, 50, and 100 μm were purchased from Dupont Co. and were used as base polymers 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.).

Isopropyl alcohol (IPA) used in electrode preparation was of reagent grade (Duksan Pharmaceutical Co., South Korea) and was used without further purification. Carbon paper was purchased from SGL Carbon group (10BC, Germany). Pt/C catalyst contained 40% of platinum over active carbon (E-T Co., USA). 5% Nafion emulsion in IPA (Nafion perfluorinated ion-

exchange resin) was purchased from Aldrich Co. (USA).

2.2 Preparation of membrane

2.2.1 Grafting of styrene monomer

The ETFE film with dimensions of 50 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 electron beam onto the ETFE film immersed into styrene monomer, the grafting was performed in a dry oven at controlled temperatures. To remove possible homo-polymers in the film, the grafted ETFE 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 around 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.

2.2.2 Sulfonation of styrene-grafted ETFE

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

The ion exchange capacity (IEC) [11] 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.

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

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.

2.3 Preparation of electrode

Manufacture of electrode was performed by the following steps: 1g of Pt/C catalysts and 100ml of isopropyl alcohol (IPA) were mixed in ultrasonic cleaner (solution A). 1g of 5% Nafion solution and 5g of IPA were mixed in ultrasonic cleaner (solution B), and finally the solutions (A) and (B) were mixed for several minutes. The mixed solution was coated on the carbon paper little by little with a sprayer, and the coated solution was dried at 80°C and then was weighted. These procedures were repeated step by step till a determined Pt content over the carbon paper was obtained. Finally, the upper layer of Pt-coated carbon paper was coated with 5% Nafion solution diluted with IPA till the dried amount was 0.25mg/cm², to give adhesiveness when the carbon papers were adhered to a polymer membrane.

2.4 Equipment for testing DMFC

This study designed and assembled the apparatus for DMFC (Photo 1 & Figure 1). Ethanol of fuel in deionized water with the concentrations of 1-6wt% entered into the anode in cell through a preheating coil,

which flow rate was controlled by a diaphragm type micro-pump. On the other hand, oxygen flowed into the cathode through preheating coil controlling its flow rate with mass-flow controller (MFC). Gas effluent from cathode passed through water absorber with silica gels to prevent a possible damage of the MFC due to condensed water that had been produced by reaction of protons and oxygen. The fuel cell and two preheating coils were equipped in a dry oven to control their operating temperature. Pressures of both anode and cathode were controlled at same value of around 0.4bar. Voltage and ampere of generated electric power was measured by changing resistance.

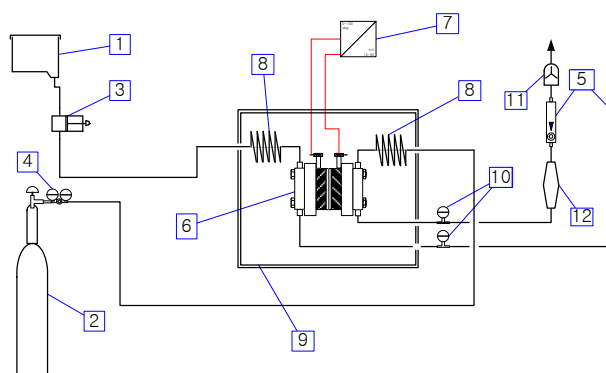


(a) DMFC cell



(b) apparatus overview

Photo 1: Photograph for DMFC equipment



1	Feeder of MeOH+H ₂ O	7	Measuring device(A/V)
2	O ₂ cylinder	8	Preheating coil
3	Metering pump	9	Constant temp. bath
4	Pressure regulator	10	Pressure guage
5	Rotameter	11	Mass flow controller
6	Fuel cell	12	Water absorber

Figure 1: Systematic drawing for experimental apparatus.

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 dose increased. At 100kGy, even five hours of grafting could give only 8.8% of grafting degree. High dose of electron beam encourage to produce many several kinds of radicals onto the polymer chains, but the number of produced radicals cannot be continually increased with dose, rather being limited above any high dose. Moreover, a too high dose can cause chain-scissions in polymer structure, probably resulting in a decrease of grafting degree.

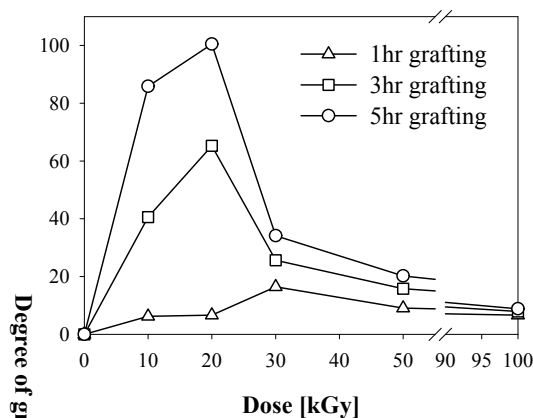


Figure 1: Degree of grafting in ETFE film according to grafting time at several doses at 45°C of grafting temperature.

3.2 Sulfonation of styrene-grafted ETFE film

Since the sulfonic acid group (SO_3H) attached to the styrene molecules is dissociated into SO_3^- 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.

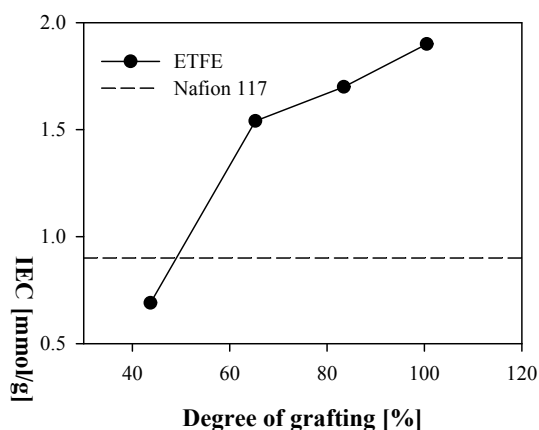


Figure 2: IEC versus degree of grafting at 20kGy of dose, 45°C of grafting time, and 3hr of grafting time.

3.3 Methanol crossover

Methanol at cathode, which is transferred from anode through membrane, was found to cause a mixed potential due to the interference of methanol oxidation with the oxygen reduction reaction, resulting in a decrease in the cell performance [12].

Figure 3 shows the crossover in ETFE membrane at several methanol concentrations ranged by 1wt% to 5wt%. As methanol concentration was higher, the methanol crossover started at earlier time. Comparing ETFE membrane with Nafion 117 membrane, the ETFE membrane could much more suppress the methanol crossover.

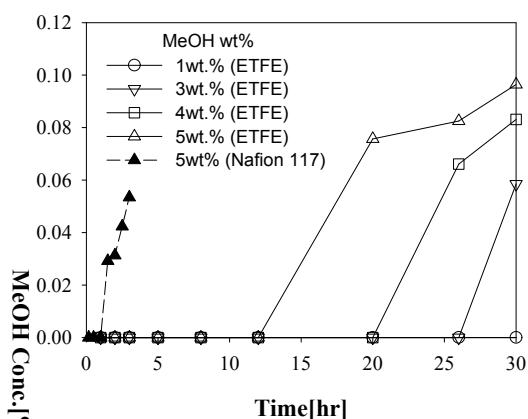


Figure 3: Effects of the MeOH concentration on methanol crossover across the sulfonated and hydrated ETFE membrane with 57.8% of grafting degree.

3.4 Fuel cell performance

Electrical characteristics of ETFE membranes prepared by radiation technology were tested in the DMFC and compared with Nafion 115. The catalysts on electrodes (anode and cathode) were consisted of 40% of platinum supported by active carbons, which were coated over carbon papers with $0.4\text{mg}/\text{cm}^2$ or $1.6\text{mg}/\text{cm}^2$. In Figure 4, fuel cell was operated with 3wt% of MeOH at several cell temperatures. Electric power generations increased with increasing cell temperature ranged by 25°C to 75°C . Comparing $0.4\text{mg}/\text{cm}^2$ and $1.6\text{mg}/\text{cm}^2$ of Pt loadings with each other, electrode with higher loading of Pt generated more electric power, but the differences of powers were ranged by about only $0.2\text{--}0.4\text{mW}/\text{cm}^2$.

Comparing $50\mu\text{m}$ and $100\mu\text{m}$ of ETFE membranes, $50\mu\text{m}$ of membrane could generate more electric power regardless of its lower grafting degree. Nafion 115 membrane was superior to ETFE membranes in the electric power generation, but $50\mu\text{m}$ of membrane was likely to generate more electric power at high cell temperature.

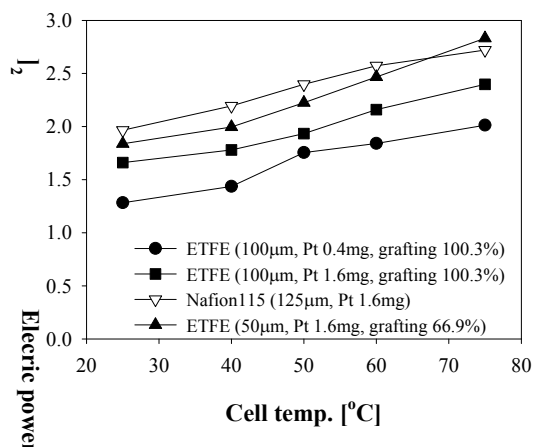


Figure 4: Comparison of electric powers generated in ETFE and Nafion 115 membranes at several cell temperatures (Load: 50Ω , MeOH: 3wt%).

As shown in Figure 5, ETFE membrane with 74.0 % of grafting exhibited slightly better electrical characteristics than 100.3% of grafting degree, even though higher degree of grafting gave higher value of IEC

(Figure 2). This might be arisen from a higher possibility of MeOH crossover at higher degree of grafting.

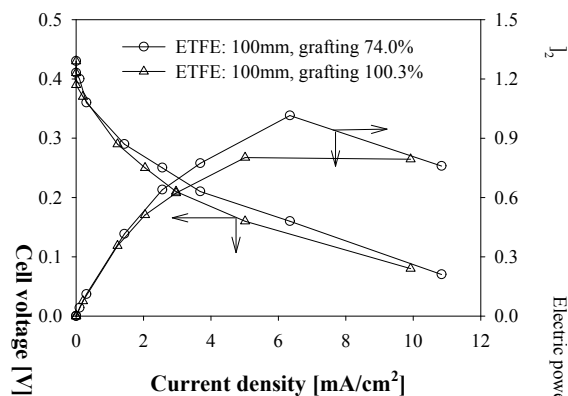


Figure 5: Current density vs. cell voltage and electric power density generated ETFE membrane ($100\mu\text{m}$) under variable resistances (Pt loading: $0.4\text{mg}/\text{cm}^2$, MeOH: 3wt%, Cell temp: 25°C).

Figure 6 shows the effect of MeOH concentration on the generation of electric power at several cell operating temperatures. Maximum electric power existed around 3wt% of MeOH, regardless of cell temperature. This might be caused by such fact that a lower concentration of MeOH can produce less numbers of protons, whereas at a higher concentration of MeOH the crossover is more dominant as shown in Figure 3 even though more numbers of protons can be produced.

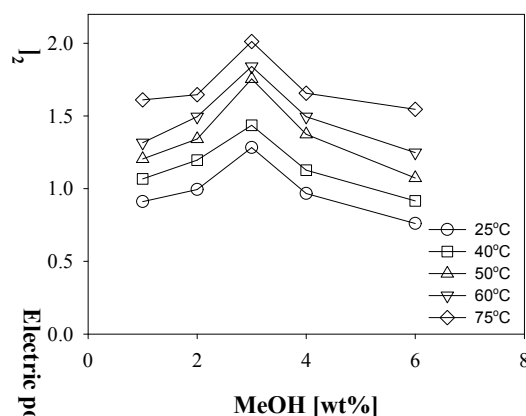


Figure 6: Effect of MeOH concentration on electric power generated on the ETFE membrane ($100\mu\text{m}$) with 97.9% grafting and $0.4\text{mg}/\text{cm}^2$ of Pt content under 50Ω load at several cell temperatures.

Figure 7 shows that, as electric power was more generated (with increasing cell temperature), the pH of effluent at anode decreased, shifting to acidic state. This might be related to the amount of produced protons (H^+ ions), i.e. as cell temperature increased the protons were more produced, resulting in a decrease of pH value.

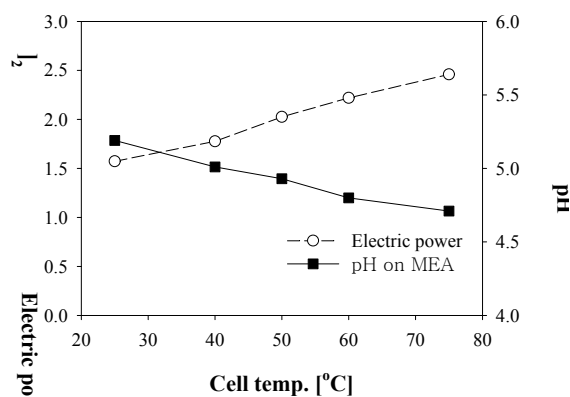


Figure 7: Changing of pH for effluent at anode during generation of electric power on 25 μ m of ETFE membrane with 1.6mg/cm² of Pt and 3wt% of MeOH under 50 Ω load.

4. CONCLUSION

This study could manufacture a good performance of ETFE membrane for DMFC by grafting styrene monomer to ETFE film with electron beam radiation technology.

The degree of styrene-grafting is strongly affected by irradiation dose, leading to a maximum degree of grafting at around 20kGy of dose and considerably lowering at high doses.

The IEC values of ETFE membranes were much higher than that of the commercialized Nafion 117. The IEC of the ETFE membrane with a degree of grafting of around 50% is equal to that of Nafion 117 (0.9 meq/g). ETFE membrane could much more prohibit the methanol crossover than Nafion membrane.

Electrode with 1.6mg/cm² of Pt loading generated more electric power than

0.4mg/cm², but the differences of power were ranged by about only 0.2-0.4mW/cm².

Comparing 50 μ m and 100 μ m of ETFE membranes, 50 μ m of membrane could generate more electric power regardless of its lower grafting degree. Nafion 115 membrane was superior to ETFE membranes in the electric power generation, but 50 μ m of membrane was likely to generate more electric power at high cell temperature.

ETFE membrane with 74.0 % of grafting exhibited slightly better electrical characteristics than in 100.3% of grafting degree, even though higher degree of grafting gave higher value of IEC. This might be caused by a higher possibility of MeOH crossover at higher degree of grafting.

Maximum electric power existed around 3wt% of MeOH, regardless of cell temperature. This might be arisen from such fact that a lower concentration of MeOH can produce less numbers of protons, whereas at a higher concentration of MeOH the crossover is more dominant.

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