

Preparation and Characterization of Poly(styrenesulfonic acid)-grafted Fluoropolymer Membrane for Direct Methanol Fuel Cell

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Abstract: A proton exchange membrane was prepared by γ -irradiation-induced grafting of styrene into poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) and subsequent sulfonation reaction. The degree of grafting (DOG) increased with an increase in the absorbed dose. The prepared membranes showed high ion exchange capacity reaching 3.0 meq/g, which exceeded the performance of commercially available perfluorosulfonic acid membranes such as Nafion. The proton conductivity of PFA-g-PSSA membrane increased with the DOG and reached 0.17 S/cm for the highest sample at room temperature. The DMFC performance of the prepared membranes with 50% DOG was comparable to that of Nafion membrane.

Keywords: radiation-induced grafting, poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA), Nafion, ion conductivity

1. Introduction

Common requirements of a polymer electrolyte membrane for direct methanol fuel cell (DMFC) applications include: (i) operation at high temperature, (ii) low methanol permeability, (iii) high proton conductivity, (iv) high chemical and mechanical durability, and (v) low cost [1]. Many fluorinated polymer-based membranes for DMFC such as Nafion, Flemion, Aciplex, and Gore-Secect have been commercialized for DMFC applications [1,2]. Although they show good DMFC performance, these membranes do not satisfy all of the above mentioned requirements. Therefore, it is necessary to develop an alternative membrane which is less expensive and has high DMFC performance. To date, the new proton exchange membranes being developing as alternatives to Nafion include hydrocarbon polymers,

acid-base polymer complexes, composite membranes, and radiation-grafted membranes [1].

Radiation-induced grafting of fluoropolymers has been reviewed by T. R. Dargaville *et al.* [3]. Radiation-induced graft polymerization is a well-established technology and does not require any initiators. This technique thus has many advantages: (i) the polymerization proceeds mildly and thoroughly, (ii) the chemistry of the reaction system is free of contamination, and (iii) the energy consumption is relatively low. There are three methods for radiation grafting: (i) simultaneous method, (ii) pre-irradiation (trapped radical) method, and (iii) peroxide method. In the simultaneous method, a polymer is irradiated in the presence of a monomer solution. Alternatively, in the pre-irradiation (trapped radical) method, polymer can be first irradiated and then subsequently immersed it in a monomer solution to start the grafting reaction. In the peroxide method, a material is irradiated in the presence of air

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in order to generate peroxides. The peroxides generated after irradiation can be activated at an elevated temperature to form radicals.

In this study, we prepared poly(styrenesulfonic acid)-grafted poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) membranes by simultaneous radiation-induced grafting of styrene followed by sulfonation reaction. Characterization of the prepared membranes was carried out by means of the measurement of the ion exchange capacity, proton conductivity, methanol permeability, and fuel cell performance.

2. Experimental

2.1. Materials

Poly(tetrafluoroethylene-perfluoropropyl vinyl ether) (PFA) films of 100 μm thickness were supplied by Universal (Japan). Styrene (purity > 99 %), HCl, and NaOH were supplied by Showa Chemical Company. Dichloromethane and dichloroethane were purchased from Junsei Chemical Company (Japan). Chlorosulfonic acid was supplied by Kanto Chemical Company (Japan). Other solvents were supplied by Duksan Chemical Company (Korea).

2.2. Preparation of Proton Exchange Membranes

PFA-g-polystyrene (PFA-g-PS) films were prepared by the simultaneous radiation-induced graft polymerization of styrene onto PFA films [4]. The PFA films were washed with acetone and dried in a vacuum oven at 60°C for 24 h prior to use. The pre-treated PFA films were immersed in a styrene/dichloromethane solution in the glass ampoule. The ampoule was irradiated using γ -rays from a ^{60}Co source to a total dose of 10 to 200 kGy at a dose rate of 10 kGy/h. The films were washed with dichloromethane several times to remove the homopolymers, and then dried in a vacuum oven at 60°C. The degree of grafting (DOG) was calculated from the equation: $\text{DOG} (\%) = (W_g - W_0) / W_0 \times 100$, where W_0 is the weight of original film and

W_g is the weight of grafted film, respectively.

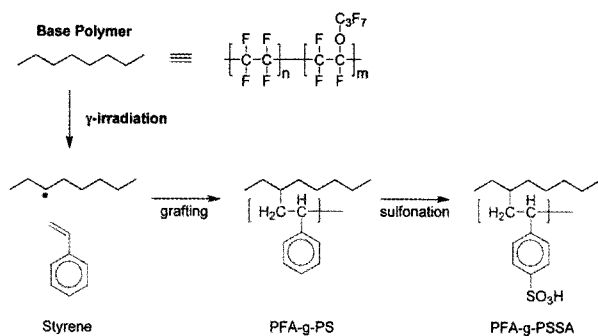
The PS grafted films were sulfonated in a chlorosulfonic acid/dichloroethane (5/95 v/v) solution at room temperature for 12 h. The sulfonated membranes were washed several times with dichloroethane to remove the excess chlorosulfonic acid, and then dried in a vacuum oven at 60°C overnight. The sulfonated membranes were treated with 0.5 M KOH solution for 1 day at room temperature. The membranes were finally regenerated into acid form by immersing into 1.0 M H_2SO_4 for 6 h. The films were then washed with deionized water several times.

2.3. Characterization of Prepared Membranes

The ion exchange capacity (IEC) of the membranes was determined by acid-base titration. The membrane samples in acid form were immersed into a 0.1 M NaOH. The excess NaOH was titrated with a 0.1 M HCl. From the volume of NaOH solution consumed in titration, the IEC of the dry membrane of per unit mass (meq/g) was calculated.

The proton conductivity of the membrane at room temperature was measured by AC impedance technique over the frequency range from 0.01 to 100 kHz using a Solatron SI 1260 frequency response analyzer combined with an SI 1287 electrochemical interface. The constant potential was 10 mV. The samples were hydrated in water overnight measurement and then hot-pressed between two carbon papers 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 samples with area of A and thickness of L were sandwiched between two carbon electrodes to measure the electrolyte resistance (R_b , Ω). The conductivity (σ , S/cm) was then calculated from the equation: $\sigma = L / (R_b A)$.

The methanol permeability of the polymer electrolyte membrane was tested in a two-reservoir diffusion cell [5,6]. In the two separate reservoirs, 5 wt% methanol solution and distilled water were added, respectively, and magnetically stirred to avoid concentration gra-



Scheme 1. Overall synthetic scheme for the preparation of PFA-g-PSSA membrane.

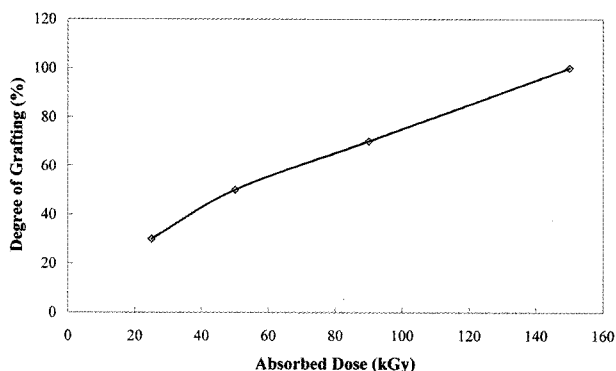


Fig. 1. Degree of grafting as a function of absorbed dose.

dients in each reservoir at room temperature. The concentration of methanol in the water-side reservoir was measured as a function of time by a gas chromatography. The methanol permeability was calculated from the Fick's law of diffusion [6].

2.4. Fuel Cell Experiments

Fuel cell performance test was carried out in 16 cm² single cell using E-TEK Pt-based electrodes. PFA-g-PSSA membranes were hot pressed between two electrodes at 100°C for 5 min. The membrane-electrode assembly (MEA) was mounted in a single cell test unit. Fuel cells were operated on 3 wt% methanol (2 mL/min) and air (200 mL/min). DMFC tests were conducted by sweeping potential and recording current.

3. Results and Discussion

The radiation grafting of styrene into PFA (PFA-g-PS) with subsequent sulfonation yields acidic proton

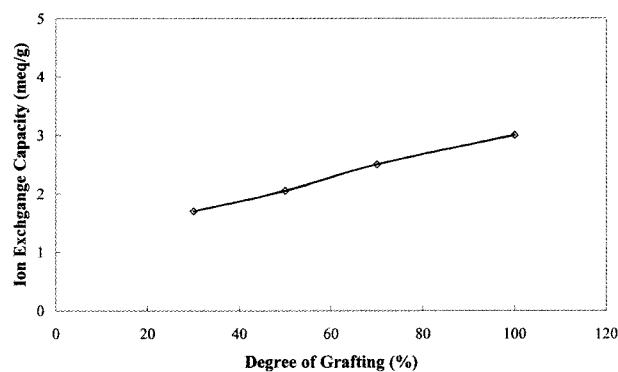


Fig. 2. Ion exchange capacity of the membranes as a function of the degree of grafting.

conducting membranes (PFA-g-PSSA, Scheme 1). In radiation grafting process, dichloromethane was used as a polymerization solvent due to its electron acceptor nature and low chain transfer constant as well as its good swelling property to the matrix [4]. The concentration of styrene was 50 vol% and the irradiation dose was in the range of 10~200 kGy at a dose rate of 10 kGy/h. The degree of grafting increased as the irradiation dose increased (Fig. 1). The polystyrene grafted films were sulfonated by a chlorosulfonic acid/dichloroethane mixture (5:95 v/v) at room temperature for 12 h in a subsequent step to introduce the sulfonic acid groups to polystyrene side chains.

Fig. 2 shows the relationship between ion exchange capacity (IEC) of PFA-g-PSSA membranes and the degree of grafting. It can be observed that IEC depended strongly on the degree of grafting. The IEC of the membranes per unit mass (meq/g) increased with increasing the DOG. This can be reasonably attributed to the increase in the number of sulfonic acid groups introduced into the membrane with an increase in the DOG [7,8]. Almost all samples had higher ion exchange capacities than Nafion 117 (0.90 meq/g) did (Fig. 2).

Fig. 3 shows the relationship between ionic conductivity and the DOG of the membranes at room temperature. The results indicate that the proton conductivity increased with the DOG up to 70% of DOG, beyond which it started to level off. The increase in the proton conductivity with the DOG is due to the

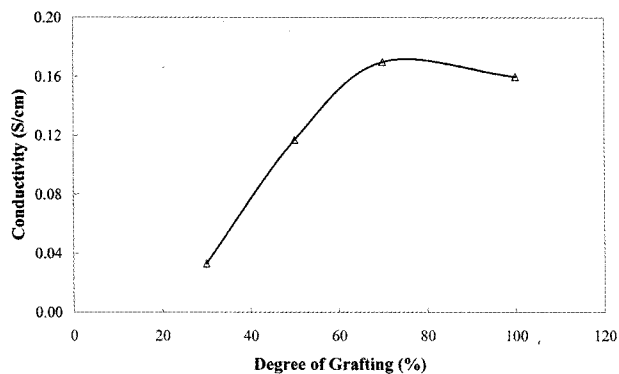


Fig. 3. Proton conductivity as a function of the degree of grafting.

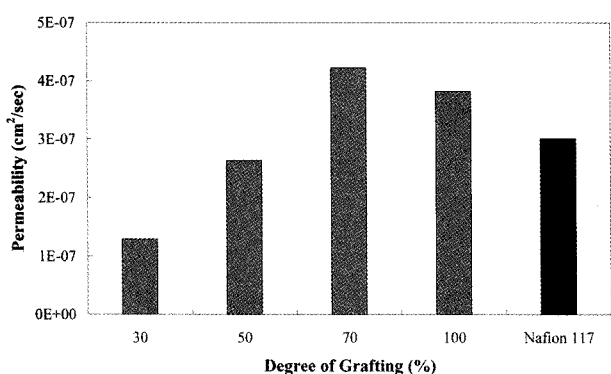


Fig. 4. Methanol permeability of PFA-g-PSSA membranes.

increase in the amount of sulfonic acid groups [7,8]. It was reported that the grafting of styrene onto fluorinated polymer film started at the surface of the film and continued to the middle by progressive diffusion of the monomer through the grafted layers. At low degree of grafting, the grafting was located near to the surface of the film, while its middle remained ungrafted and subsequently exerted simultaneous higher internal resistance and low ionic conductivity. As grafting reached the middle of the film, the internal resistance vanished and, consequently, the ionic conductivity increased. Further an increase in the degree of grafting did not bring considerable increases in the proton conductivity due to the achievement of homogenous distribution of sulfonated polystyrene grafts in the membrane [7,8]. The membranes exhibited high ionic conductivity at room temperature reaching 0.17 S/cm for the highest conducting sample and better ionic conductivity than Nafion 117 (0.08 S/cm).

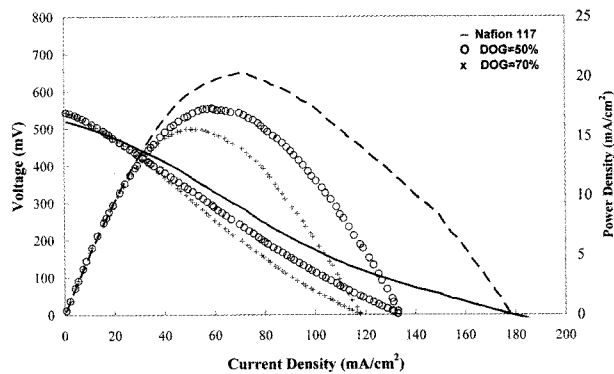


Fig. 5. DMFC performance of PFA-g-PSSA membranes.

Fig. 4 shows the methanol permeability of the PFA-g-PSSA and Nafion 117 membranes. The methanol permeability increased with increasing the DOG up to 70%, beyond which it tended to level off [9]. These results were in line with the results of proton conductivity measurements. The increase in the methanol permeability could be reasonably attributed to the increased amount of sulfonic acid groups followed by the increase in the water uptake [7,8]. The decrease in the methanol permeability could be ascribed to the increased membrane thickness upon grafting. As the DOG increased, the membrane thickness increased and it could limit the methanol permeability [9].

Fig. 5 compares the DMFC performances (cell voltage versus current density) of Nafion 117 and PFA-g-PSSA membranes. The DMFC performance of PFA-g-PSSA membrane having 50% DOG was comparable to that of Nafion 117 membrane. The peak power density of Nafion and PFA-g-PSSA (DOG: 50%) membranes was 20.3, and 17.0 mA/cm², respectively. The DMFC performance of the PFA-g-PSSA membrane (DOG: 50%) was better than that of the PFA-g-PSSA membrane (DOG: 70%) because of lower methanol permeability of the membrane with lower DOG [9].

4. Conclusion

PFA-g-PSSA membranes for DMFC application were successfully prepared by simultaneous radiation-induced grafting of styrene into PFA and followed by sulfonation reaction. The ion exchange capacity, proton con-

ductivity, and methanol permeability increased with increasing the degree of grafting. The proton conductivity of PFA-g-PSSA membrane reached 0.17 S/cm for the highest sample at room temperature. The DMFC performance of the PFA-g-PSSA membrane with 50% DOG was comparable to that of Nafion membrane. Additional work is underway to optimize the composition of the grafted polymer (e.g., styrene/divinylbenzene) and to test the DMFC performance including the membrane durability.

Acknowledgement

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