Communications

Modified Sulfonated Poly(arylene ether sulfone) Membranes Prepared via a Radiation Grafting Method for Fuel Cell Application

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Introduction

Polymer modifications involving crosslinking and grafting by radiation have been widely researched for use in biopolymers, hydrogels, heat-resisting electric wires, vulcanization, polymer recycling, gas separation, and pervaporation membranes because of their advantages over traditional chemical crosslinking and grafting methods, including a catalyst-free reaction, post-modification at room temperature for solid polymers, and short modification times and steps.[1-8] Various recent studies have also utilized radiation modification techniques to prepare proton exchange membranes (PEMs).[3,9-12]

PEMs are membranes which have the ability to selectively transfer protons generated by electrochemical reactions from the anode to the cathode in fuel cells. For this purpose, polymers having strong acidic functional group as

proton carriers (e.g. sulfonic acid groups) have generally been used. There are two main strategies to introduce sulfonic acid groups into polymers.[13,14] One is to introduce the groups directly to a polymer (post-sulfonation or polymer-sulfonation) and the other is to perform polymerization with a sulfonated monomer (monomer-sulfonation). To date, pre-irradiation and post-sulfonation methods, in which sulfonic acid groups are introduced after crosslinking or grafting non-sulfonated polymers by irradiation, have been used in radiation-induced processes of PEMs in order to prevent unfavorable membrane damage such as decomposition of sulfonic acid groups.[3,9,15] However, this method has structural limitations for PEMs because the types of target polymer for irradiation are restricted to perfluorinated or partially fluorinated polymers and aliphatic polymers. In addition, crosslinking and grafting agents should have sites available for post-sulfonation.[3,9] Whereas, few studies have been conducted on radiation-induced sulfonated polymers (post-irradiation method) despite the advantage that various types of polymers, prepared with various sulfonated and non-sulfonated monomers, can be used as a matrix for radiation modification.[4,10]

In this study, we investigated a post-irradiation method for PEMs and tried to improve PEM performance by preparing a radiation-grafted sulfonated polymer. Sulfonated polyarylene ether sulfone (SPAES) was used as a polymer matrix for irradiation. Here, the sulfonated polymer with a perfluorinated backbone (e.g. Nafion®) was excluded due to its serious decomposition resulting from the chain scission effect caused by irradiation.[15] Due to its additional acid group, acrylic acid was used as a grafting agent to increase the proton conduction properties of the resulting polymer.

Results and Discussion

Sulfonated poly(arylene ether sulfone) (SPAES) membranes grafted with acrylic acid were successfully prepared by the radiation method illustrated in Scheme I. SPAES membranes with a 40% degree of sulfonation (DS) were thoroughly swollen as grafting matrix for irradiation in an acrylic acid/water/methanol mixture to effectively penetrate

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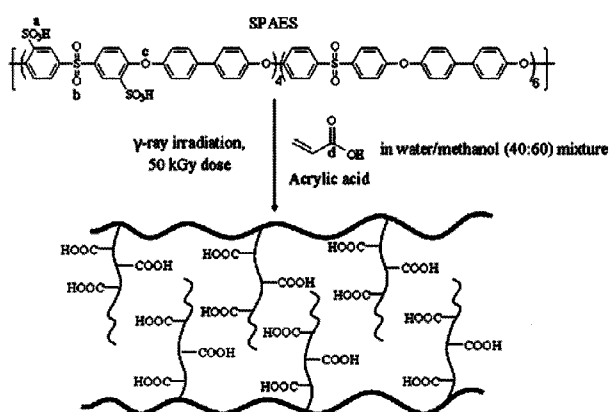
Scheme I. Radiation grafting of poly(acrylic acid) into sulfonated poly(arylene ether sulfone) (SPAES).

acrylic acid into the hydrophilic channels. Pristine SPAES membranes in their sodium salt form (-SO$_3$Na) and protonated form (-SO$_3$H) were compared to investigate the structural effect of sulfonic acid groups on radiation grafting. In addition, 10 wt% and 20 wt% acrylic acid solutions were used to study the effect of grafting agent concentration on the grafting ratio.

Figure 1 shows the ATR-FTIR spectra of the resulting radiation-grafted SPAES membranes obtained for the structural analysis. The whole membrane samples show no significant difference in (a) peaks (1030 cm^{-1} and 1098 cm^{-1}) assigned as sulfonic acid groups. They also show very similar shapes of (b) peaks (1149 cm^{-1} and 1320 cm^{-1}) and (c) peaks (1006 cm^{-1} and 1234 cm^{-1}) assigned as the sulfone and the ether linkages of the polymer backbone, respectively. These results indicate that decomposition of the poly-
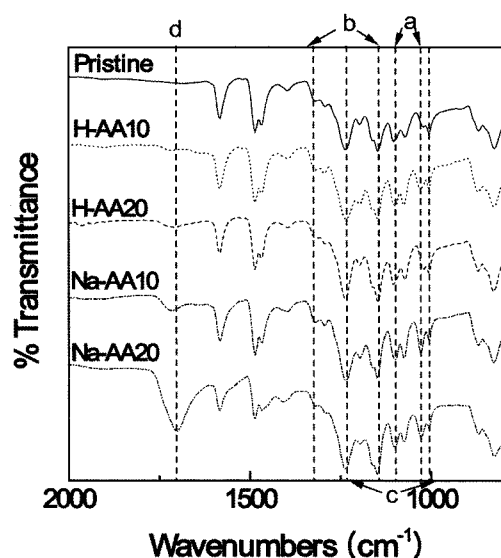
Figure 1. ATR-FTIR data of pristine SPAES and radiation-grafted SPAES membranes: (a) sulfonic acid group, (b) sulfone group, (c) ether group, and (d) carbonyl group.

mer matrix by irradiation was not a serious problem, which are further supported by ^{1}H NMR data in Supplementary Information. For radiation-grafted SPAES membranes, the (d) peak (1720 cm^{-1}) assigned as the carbonyl group of acrylic acid is clearly observed, whereas the pristine SPAES did not have a peak in that region. In particular, SPAES membranes irradiated in their sodium salt form (Na-AAxx) show a stronger adsorption band than those in their protonated form (H-AAxx). A higher concentration of acrylic acid (20 wt%) resulted in a higher grafting ratio of the resulting membranes (X-AA20). These behaviors were quantitatively confirmed by measuring the weight change of the samples before and after irradiation in Table I and by calculating the integral ratios of ^{1}H NMR data in Supplementary Information. Consequently, the largest amount of acrylic acid was grafted into the matrix when SPAES membranes in the sodium salt form were irradiated with the 20 wt% acrylic acid mixture (Na-AA20). There was not a large difference in the grafting ratios of the SPAES membranes irradiated in their protonated form (H-AA10 and H-AA20 with 10 wt% and 20 wt% acrylic acid mixtures, respectively). In general, radiation grafting is affected by the diffusion of the grafting agent into the polymer matrix.[16] For SPAES membranes in their protonated form, which bring about an anionic charge by releasing protons of their sulfonic acid groups into the methanol/water mixture, acrylic acid with the same anionic charge has difficulty diffusing into the SPAES matrix. However, in SPAES membranes in the sodium form, where sodium ions neutralize the anionic charge by ionic bonding with sulfonic acid groups, acrylic acid can easily diffuse into the SPAES matrix. In addition, acrylic acid is easily homopolymerized because it is a reactive monomer possessing radiation-sensitive properties.[3] As a result, the grafting rate of radiation-grafted SPAES membranes is dependent on the concentration of acrylic acid.

Table I shows the basic properties of the SPAES membranes used in this study. The acrylic acid used as a grafting agent is very hydrophilic and, as a result, radiation-grafted SPAES membranes with acrylic acid groups have relatively high water swelling characteristics compared to pristine SPAES. The Na-AA10 and Na-AA20 membranes radiation-grafted in their sodium form, into which relatively high amounts of acrylic acid are introduced, had much higher water uptakes and dimensional changes than the H-AA10 and H-AA20 membranes radiation-grafted in their protonated form. In particular, Na-AA20, grafted with too much acrylic acid, had drastically reduced mechanical stability under both dry and hydrated conditions, as well as problems with high water uptake and dimensional change. Due to these issues, it was impossible to measure the elongation and tensile strength of Na-AA20. H-AA10 and H-AA20 with a low grafting ratio showed similar mechanical properties as the pristine SPAES. These results demonstrate the conclusion from the ATR-IR and NMR data that decomposition prob-

Table I. The Properties of Pristine SPAES and Radiation-Grafted SPAES Membranes

Sample	Degree of Grafting^a(wt%)	Water Uptake^b		Dimensional Change^c		Tensile Strengh (MPa)	Elongation (%)	MeOH Permeability ($\times 10^{-6}$ cm^2 s^{-1})
		30 °C (%)	80 °C (%)	30 °C (%)	80 °C (%)			
Pristine	-	52.88	91.24	41.35	62.8	57.6	17.6	0.66
H-AA10	3.02	84.25	136.98	75.85	115.2	58.80	19.01	2.24
H-AA20	4.24	85.41	149.87	69.56	117.64	58.80	16.37	1.87
Na-AA10	10.04	147.17	275.14	98.57	168.7	44.90	10.98	3.3
Na-AA20	14.39	191.75	NA^d	130.23	NA^d	NA^d	NA^d	NA^d

^{a}Degree of grafting(wt%) = (($M_{grafted}$ - $M_{pristine}$)/$M_{pristine}$)×100. $M_{grafted}$ and $M_{pristine}$ are weights after and before grafting. ^{b}Water uptake(%)=((M_{wet}-M_{dry})/M_{dry})×100. M_{wet} and M_{dry} are weights of wet and dry samples. ^{c}Dimensioal stability(%)=((A_{wet}-A_{dry})/A_{dry})×100. A_{wet} and A_{dry} are areas of wet and dry samples. ^{d}For Na-AA20, tensile strength, elongation and MeOH permeability could not measured.
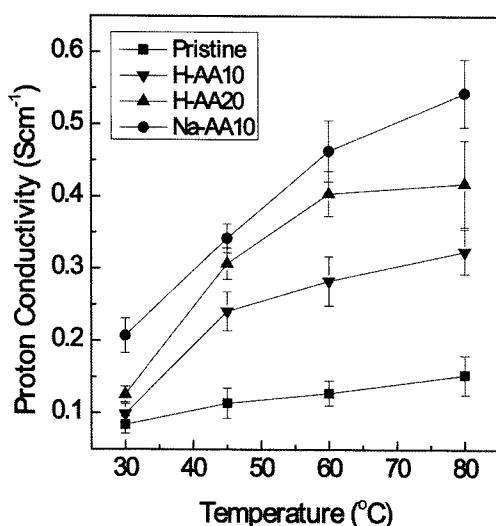
Figure 2. Proton conductivity of pristine SPAES and radiation-grafted SPAES membranes in liquid water.

lems due to irradiation are not serious in the SPAES matrix. In general, methanol permeability is proportional to water uptake and dimensional change.[17] The same results were observed in this study except for Na-AA20, which had poor mechanical stability.

The proton conductivities of the radiation-grafted SPAES membranes are shown in Figure 2. Two proton conduction mechanisms have been widely accepted.[18-20] One is the Grotthus mechanism in which protons are transported by the making and breaking of hydrogen bonding with proton carriers (i.e., hopping) and the other is the vehicle mechanism in which protons are transported with water molecules in forms such as H_3O^+, $H_5O_2^+$, and $H_9O_4^+$. In particular, the water uptake of PEMs is a very important factor to estimate their proton conductivity by the vehicle mechanism. In this study, Na-AA10, which had the highest water uptake, showed the highest proton conductivity. The proton conductivity of Na-AA20 could not be measured due to its poor mechanical stability in the hydrated state. The proton conductivities of H-AA10 and H-AA20 were proportional to their water
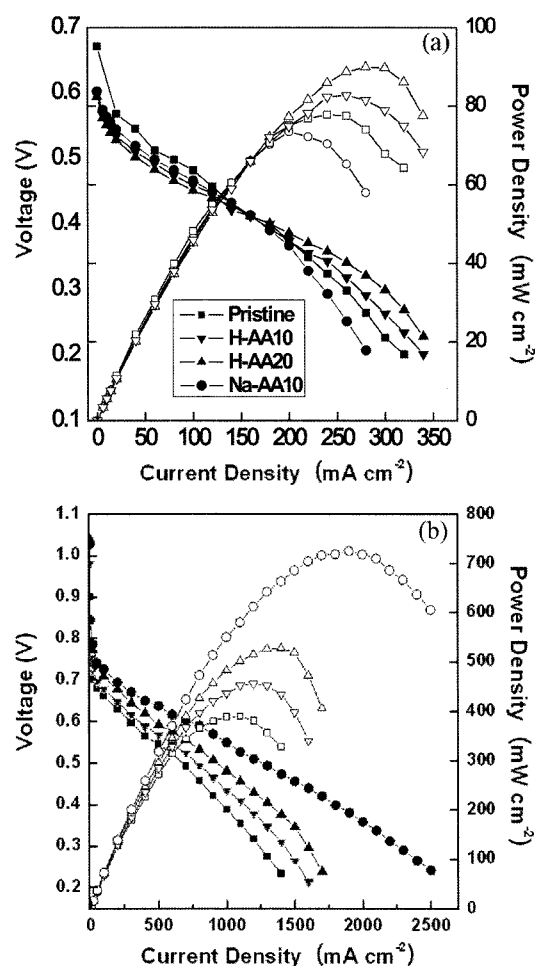
Figure 3. Fuel cell performances of pristine SPAES and radiation-grafted SPAES membranes at 80 °C. Anode: (a) 1 mL min^{-1} of 1 M MeOH (DMFC)/(b) 200 mL min^{-1} of O_2 (PEMFC). Cathode: (a)/(b) 200 mL min^{-1} of O_2 (DMFC/PEMFC), RH 100%.

uptakes.

Figure 3(a) shows the results of DMFC single cell testing using radiation-grafted SPAES membranes. Pristine SPAES with much lower methanol permeability exhibited the highest open circuit voltage (OCV), but the fastest performance drop

with increasing current density due to lower proton conductivity. Despite the highest proton conductivity, Na-AA10 had the lowest maximum power density due to its high dimensional change and methanol permeability. Consequently, H-AA20 with an appropriately high proton conductivity and low methanol permeability had the highest maximum power density, which was 15.6% higher than that of pristine SPAES.

The effect of radiation-grafting is more remarkable in PEMFC performances (Figure 3(b)) which is dominantly affected by proton conductivity. Here, the negative effect of methanol permeability can be negligible because hydrogen is used as a fuel in PEMFC. As a result, Na-AA10 with highest proton conductivity shows the highest performance, which is much higher (186% higher) than that of pristine SPAES.

In summary, we investigated the possibility of a post-irradiation technique for SPAES membranes grafted with acrylic acid. Beyond the general expectation, there was no significant decomposition of the resulting polymers, including sulfonic acid groups. The amounts of acrylic acid grafted into the SPAES matrix were affected by the form of the sulfonic acid groups of SPAES, as well as the concentration of the acrylic acid mixture. Radiation grafting of acrylic acid affected water uptake, dimensional change, methanol permeability, and proton conductivity. Consequently, optimized radiation grafting conditions improved the fuel cell performance of the resulting SPAES membranes.

Supporting Information: Experimental procedures for the synthesis and irradiation of radiation-grafted sulfonated poly(arylene ether sulfone) and ^{1}H NMR data are available *via* the Internet at http://www.polymer.or.kr.

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