

Electrochemical Properties of Polyethylene Membrane Modified with Sulfonic and Phosphonic Acid Groups

Seong-Ho Choi and Young Chang Nho[†]

Radioisotopes/Radiation Application Team, Korea Atomic Energy Research Institute, Taejeon 305-600, Korea
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Abstract—Ion-exchange membranes modified with sulfonic ($-\text{SO}_3\text{H}$) and phosphonic acid ($-\text{PO}_3\text{H}$) groups were prepared by radiation-induced grafting of glycidyl methacrylate (GMA) onto polyethylene (PE) films and sub-sequent sulfonation and phosphonation of poly(GMA) graft chains. The surface area, thickness and volume of grafted PE film increased with increasing grafting yield. The specific electrical resistance of PE membrane modified with the $-\text{PO}_3\text{H}$ and $-\text{SO}_3\text{H}$ groups decreased with increasing the ion-exchange capacity. The PE membrane modified with $-\text{PO}_3\text{H}$ group had a lower specific electrical resistance than that of PE membrane modified with $-\text{SO}_3\text{H}$ group.

Key words: Ion-exchange Membrane, Radiation-induced Graft Copolymerization, Glycidyl Methacrylate, Sulfonation, Phosphonation, Specific Electrical Resistance

INTRODUCTION

Ion-exchange membranes have been widely used in various industrial fields. Their electrochemical properties such as transport number, electrical resistance, etc. have been vastly improved. At the same time, ion-exchange membrane is a typical functional polymer and can be used not only as a separation membrane, but also as a new functional material. Ion-exchange membranes have been made by many workers [Kaboi et al., 1996; Kubota et al., 1996; Moharram et al., 1997; Roboiras, 1996; Tasaka et al., 1997], and efforts to find new applications should be continued.

In recent years, radiation-induced graft polymerization has been an important research subject, because it is a good method for the modification of chemical and physical properties of polymeric material. In order to obtain various kinds of functional polymers, grafting of monomers containing different types of functional group or those which are easily modified to functional groups should be tried. Glycidyl methacrylate (GMA) is one of the monomers easily modified into various functional groups. After GMA is polymerized, the epoxy groups of poly(GMA) are changable to alcohols [Kim et al., 1996], amines [Choi et al., 1998], phosphonic acid [Saito et al., 1989], etc. [Kiyohara et al., 1996]. In our previous works [Choi et al., 1998], we selected phosphonic ($-\text{PO}_3\text{H}$) and sulfonic ($-\text{SO}_3\text{H}$) acid groups among the ion-exchange groups suitable for removal of heavy metal ions. Also, we prepared the ion-exchange membranes containing carboxylic acid group for battery separator by radiation-induced grafting of acrylic acid and methacrylic acid onto a polyethylene film. These membranes showed a high electric flux and electrical conductivity [Choi et al., 1998]. These results led to the study of the electrical properties of polyethylene membranes modified with sulfonic and phosphonic acid

groups.

In this study, ion-exchange membranes were prepared by radiation-induced grafting of glycidyl methacrylate (GMA), and subsequent sulfonation and phosphonation of poly(GMA) graft chains. Electrochemical properties such as electrical resistance and transfer number of the ion-exchange membranes were examined.

EXPERIMENTAL

1. Materials

Polyethylene (PE) films of thickness 0.03 mm were purchased from Tae-Syeng Chemistry Co. (in Korea), washed with methanol and dried in a vacuum oven at 50 °C for 8 h. Reagent-grade glycidyl methacrylate [$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CHOCH}_2$, GMA] was used as received from Aldrich. All the other chemicals of reagent grade were used without further purification.

2. Grafting Procedure

Scheme 1 shows the preparation procedure of radiation-induced grafting of GMA onto PE film. The PE film was used as the base polymer for grafting polymerization. PE film of size 4×5 cm was irradiated by γ -ray from Co-60 under atmospheric pressure and ambient temperature, and then reacted with monomer. The unreacted monomer and homopolymers after grafting of GMA were removed with tetrahydrofuran (THF). PE film obtained by grafting copolymerization was dried in a vacuum oven at 60 °C for 7 h. For the studies of the effects of various parameters on the grafting copolymerization, the degree of grafting is defined as

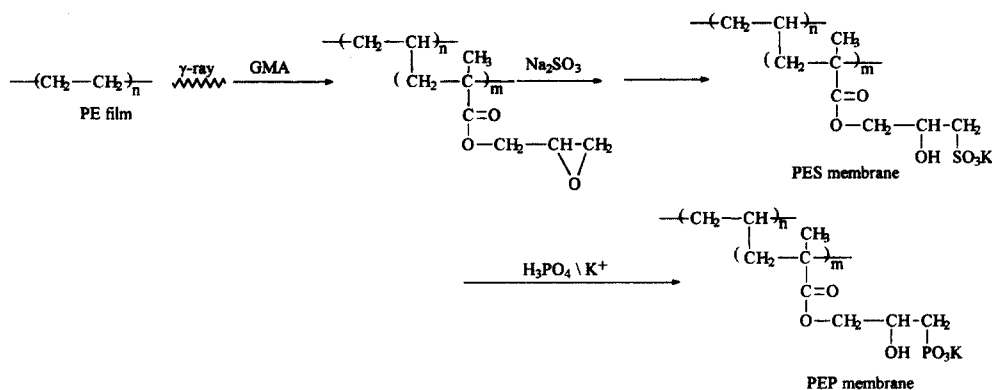
$$\text{Degree of grafting (\%)} = [(W_g - W_o) / W_o] \times 100 \quad (1)$$

where W_g and W_o denote the weights of the grafted and the ungrafted PE film, respectively.

3. Sulfonation of GMA-grafted PE Film

Epoxy group of GMA-grafted PE film was converted into $-\text{SO}_3\text{Na}$ group by immersing GMA-grafted PE film in sulfonat-

[†]To whom correspondence should be addressed.
E-mail: choish@nanum.kaeri.re.kr



Scheme 1. Preparation of two cation-exchange membrane.

ing reagents as reported earlier [Choi et al., 1998]. After sulfonation, the membrane was converted into H form by treating with 1.0 M HCl. The $-\text{SO}_3\text{H}$ group content was determined from the measurement of total ion-exchange capacity by titration. H-form membrane was immersed in 5% NaCl aqueous solution at room temperature for 12 h, and then the hydrogen ion liberated from the membrane was titrated with 0.025 N NaOH aqueous solution.

4. Phosphonation of GMA-grafted PE Film

Epoxy group of GMA-grafted PE film was converted into $-\text{PO}_3\text{H}$ group by immersing GMA-grafted PE film in 85% H_3PO_4 aqueous solution. The $-\text{PO}_3\text{H}$ group content was determined from the measurement of total ion-exchange capacity by titration. H-form membrane was immersed in 5% NaCl aqueous solution at a room temperature for 12 h, and then the hydrogen ion liberated from the membrane was also titrated with 0.025 N NaOH aqueous solution.

5. Electrical Resistance

The electrical resistance of the grafted film was measured in 1.0 M KCl solution at 25 °C using an IM5-D impedance measurement apparatus working at 1,000 Hz. The specific electrical resistance, R_{sp} (Ω cm) was calculated by the next equation:

$$R_{sp} = \{[(R_{\text{soln+membr}} - R_{\text{soln}})] / T\} \times S \quad (2)$$

where $R_{\text{soln+membr}}$ denotes the electrical resistance of KCl solution in the presence of membrane, and R_{soln} denotes the electrical resistance of KCl solution without membrane. T and S are the thickness and surface area of the membrane.

6. Transport Number (t_+)

The grafted film was conditioned in 0.75 N KCl solution for 1 day at room temperature and then placed in between two compartments. KCl solutions of 0.5 and 1.0 N were made to flow separately through the membranes until equilibrium was reached. The membrane potential was measured at 25 °C using IM5-D impedance measurement. The transport number (t_+) of counterions in the membrane was calculated from the value of the measured potential (E_m) by the following equation:

$$t_+ = E_m / 2E_0 + 0.5 \quad (3)$$

where E_0 is the theoretical potential calculated by the Nernst equation

$$E_0 = RT/F \ln(C_2\gamma_1/C_1\gamma_2) \quad (4)$$

where γ_1 and γ_2 are the activity coefficients of KCl at concentration C_1 and C_2 , respectively.

RESULTS AND DISCUSSION

1. Grafting of GMA

In pre-irradiation grafting, the polyethylene (PE) film was first irradiated in air, leading to the formation of free radicals mainly and some peroxides. Monomer, with or without solvent, was then reacted with the trapped free radicals and the activated peroxy trunk polymer at elevated temperature to form a graft polymer.

Table 1 shows the effects of GMA concentration and reaction time on the individual grafting of GMA onto PE film. The sample was irradiated with 100 kGy in air. The grafting yield increased with increasing reaction time. The maximum grafting was found in 6.30 M monomer concentration corresponding to the Trommsdorff effect [Chapiro A., 1962; Choi et al., 1998]. Generally, the extent of grafting depends on the solvent, the polarity of monomer, the substrate, and the concentration of monomer. Among them, the concentration of monomer is one of the most important factors because it affects the grafting yield and Trommsdorff effect. The grafted samples were characterized by IR spectroscopy as shown in Fig. 1. The infrared spectra of original PE film and GMA-grafted PE film were compared. In the IR spectrum of GMA-grafted PE film, a characteristic peak at $1,730\text{ cm}^{-1}$ assigned to carbonyl group of po-

Table 1. Effects of GMA concentration and reaction time on the individual grafting of GMA onto PE film in Me-OH^a

GMA concentration (M)	Degree of grafting (%)				
	0.5 h	3.0 h	14 h	24 h	48 h
Neat	1.7	2.3	2.4	2.9	2.8
6.30 M	3.0	4.6	10.2	20.2	26.8
5.85 M	1.8	3.2	6.8	18.4	24.5
5.40 M	0.9	2.1	4.6	9.3	10.2
4.95 M	1.4	1.2	2.8	6.4	8.6
4.50 M	-0	0.8	2.4	4.5	4.7

^a Irradiation dose 100 kGy, PE film 0.03 mm, at 50 °C.

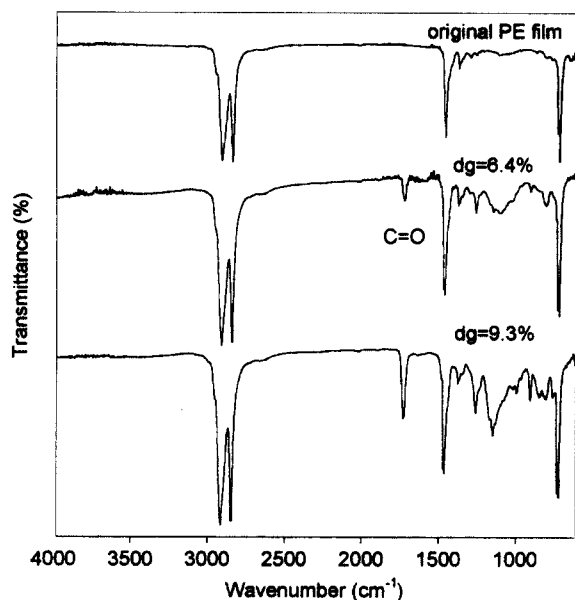


Fig. 1. FTIR-ATR spectra of original PE film and GMA-grafted PE film.

ly(GMA) was observed. On the other hand, no such peak was observed in IR spectrum of original PE film.

In order to increase the grafting yield, the grafting polymerization was performed in the presence of H_2SO_4 as an additive, because mineral acid has already been known to increase radiation grafting yield in a variety of backbone polymers [Choi et al., 1998; Dworjanyan et al., 1987; Haddadi-Asl et al., 1995]. In preparative, this concept is valuable since, in the presence of acid, lower radiation dose is required to achieve a particular percentage graft. Mechanistically, the enhancement effect by acid in grafting has been attributed to a partitioning phenomenon [Garnett et al., 1980, 1990]. Table 2 shows the effect of GMA concentration and sulfuric acid concentration on the individual grafting of GMA onto PE film. The grafting yield increased with increasing H_2SO_4 concentration.

Fig. 2 shows the infrared spectra of GMA-grafted PE film in the presence of H_2SO_4 , based on data. The prominent bands of original PE film at $1,471\text{ cm}^{-1}$, $1,351\text{ cm}^{-1}$, and 724.3 cm^{-1} , arise from $-CH_2-$ group in the chain were appeared. The strong ab-

Table 2. Effects of GMA and sulfuric acid concentration on the individual grafting of GMA onto PE film^{a)}

GMA concentration (M)	Degree of grafting (%)			
	No H_2SO_4	0.05 M H_2SO_4	0.1 M H_2SO_4	0.2 M H_2SO_4
Neat	1.7	-	-	-
6.30 M	3.0	16.8	12.8	89.3
5.85 M	1.8	9.5	13.9	37.5
5.40 M	0.9	2.0	9.0	14.0
4.95 M	1.4	~0	4.0	4.0
4.50 M	~0	~0	~0	~0

^{a)} Irradiation dose 100 kGy, PE film 0.03 mm, reaction time 0.5 h, at 50 °C, in MeOH.

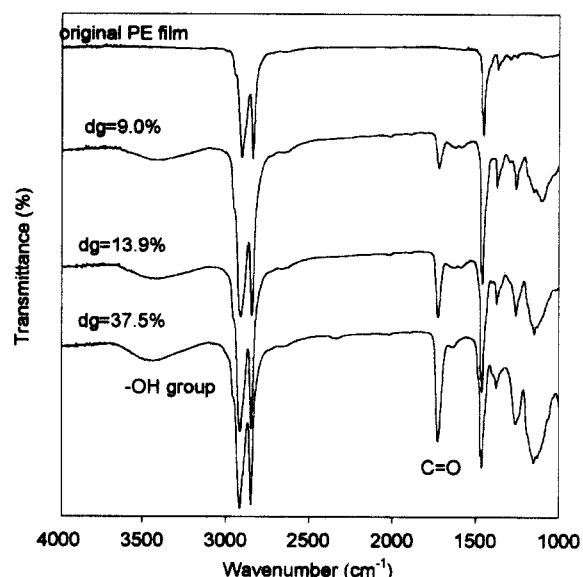


Fig. 2. FTIR-ATR spectra of original PE film and GMA-grafted PE film in Table 2.

sorption of GMA-grafted PE film obtained in the presence of sulfuric acid at about $1,730\text{ cm}^{-1}$ ($C=O$ stretching), the weak broad band at about $1,250\text{ cm}^{-1}$ (coupling of $C-O$ -stretching and $-OH$ in plane bending), and broad band at about $3,450\text{ cm}^{-1}$ ($-OH$ stretching) appeared. In the polymerization of glycidyl methacrylate in the presence of sulfuric acid, the IR spectrum of graft copolymer also exhibits a characteristic band at around $3,450\text{ cm}^{-1}$, while the graft copolymer obtained in the polymerization of GMA without sulfuric acid does not show such a band (see in Fig. 1). This may suggest that the GMA was converted to diol group in the presence of sulfonic acid. Kim et al. [1996] reported that an hydroxyl or diol group was introduced into a porous hollow fiber membrane by radiation-induced

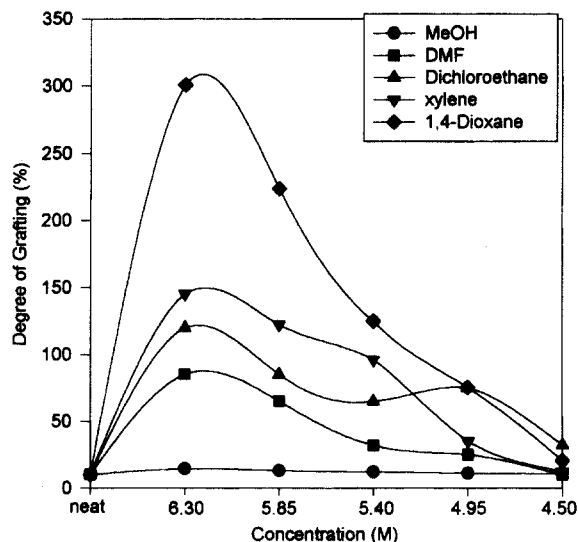
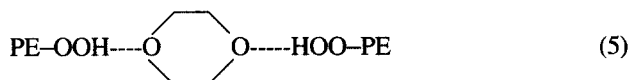


Fig. 3. Effects of solvents and monomer concentration on the grafting of GMA onto PE film preirradiated to a total dose 100 kGy at 50 °C for 3 hrs.

grafting of vinyl acetate and GMA followed by saponification or acid hydrolysis. He found that the epoxide group of the GMA-graft chains was converted into the diol group by immersing the GMA-grafted hollow fiber in 1.0 M sulfuric acid at 30 °C for 48 h.

Fig. 3 shows the effect of GMA concentration and solvents on the individual grafting of GMA onto PE film. The effect of solvents on the grafting may be attributed to two factors: (i) the extent swelling of the film in the solvent, and (ii) the degree of homopolymerization during grafting. The use of *N,N*-dimethylformamide (DMF), 1,4-dioxane, dichloroethane, xylene as diluent increased graft yield with increasing monomer concentration. Solvent effect is extremely important in radiation grafting of polyethylene since not only the efficiency of the copolymerization is affected, but also the possible appearance of a Tromsdorff peak can give the high grafting yield.

When 1,4-dioxane was used as a diluent, the degree of grafting was the highest among those used in this study. With 1,4-dioxane, another factor comes to play a role that may influence grafting. PE-OOH is capable of forming H-bonding with dioxane as following Eq. (5):



The complex would undergo decomposition to generate free radical species which may influence grafting. In the presence of CH_3OH grafting occurs without any accelerating effect. This is explained by the fact that in the presence of CH_3OH , various chain transfer and hydrogen abstraction reaction are accelerated, leading to a decrease in grafting. Different solvents show the following reactivity order in radiation induced graft copolymerization of glycidyl methacrylate onto PE film:

1,4-dioxane > xylene > dichloroethane > DMF > MeOH

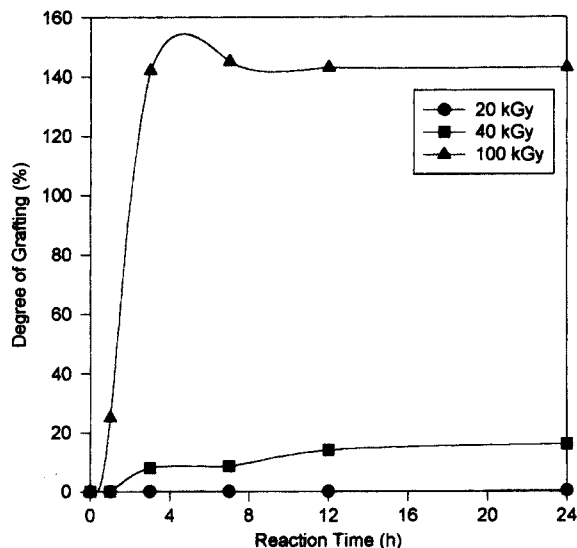


Fig. 4. Effects of irradiation dose and reaction time on the grafting of GMA onto preirradiated PE film at 50 °C in 1,4-dioxane; monomer concentration=5.40 M.

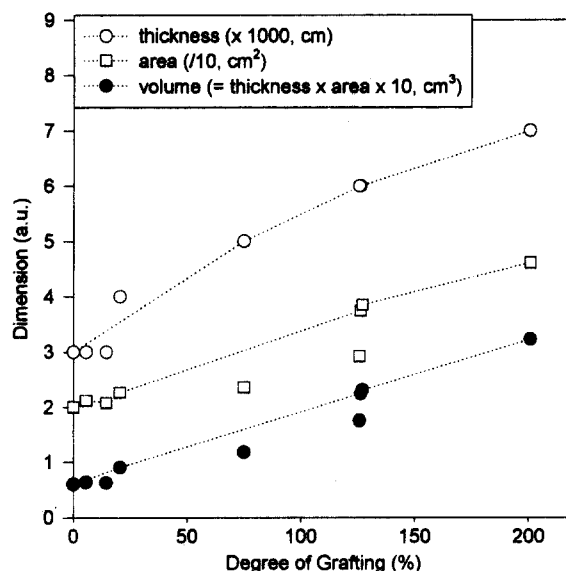


Fig. 5. Change of dimension of the PE-g-GMA.

Fig. 4 shows the effects of the reaction time and pre-irradiation dose on the individual grafting of GMA onto PE film in 1,4-dioxane at 50 °C. The grafting yield increases with increase in reaction time and irradiation dose.

Fig. 5 shows the change in dimension of the polymer film with grafting. Both the thickness and the surface area of the film increased linearly with increasing grafting yield. These increases are due to the growth of graft chains inside the polymer film as the graft polymerization occurs mainly in the amorphous region of the film, the growing of the graft chain expands the amorphous region of the film. In other words, the grafting and the resultant expansion of the trunk polymer occur mainly at the mechanically weak part of the trunk polymer.

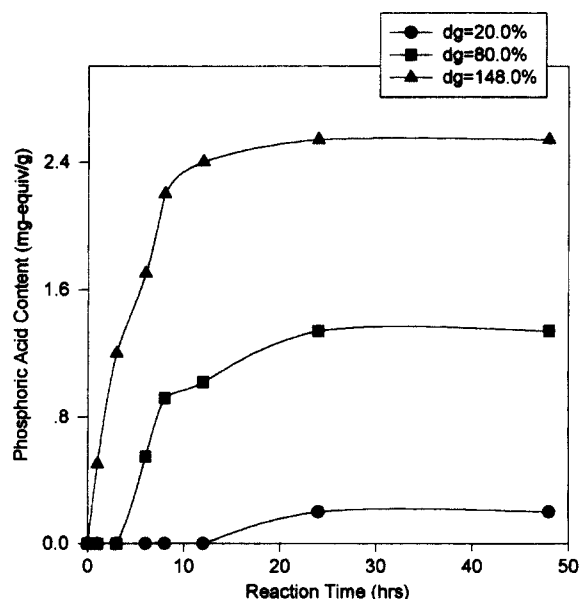


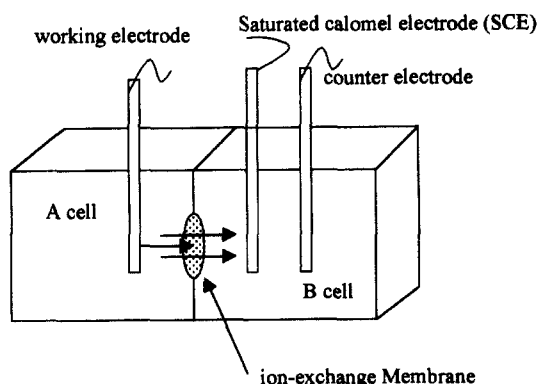
Fig. 6. Extent of phosphonation on GMA-g-PE film with 85% H_3PO_4 aqueous solution at 80 °C.

The grafted polymer composed of hydrophobic poly(GMA) grafted chain does not sorb water until the epoxy groups of the grafted chains are converted to sulfonic acid and phosphonic acid. Phosphonic acid was used GMA-grafted PE films to make ion-exchange membrane containing $-\text{PO}_3\text{H}$ group, varying modification condition such as reaction time.

Fig. 6 shows the effects of reaction time on the content of phosphonic acid using 85%-phosphonic acid aqueous solution at 80 °C for 1, 3, 7, 12, 24, and 48 h. The phosphonic acid content increases to the 9 h, and then levels off. The phosphonic acid content increases with increases in grafting yield.

2. Electrical Properties of PE Membrane Modified with $-\text{SO}_3\text{H}$ and $-\text{PO}_3\text{H}$ Groups

As the film was preliminarily conditioned with KCl solution overnight, the sulfonic acid and phosphonic acid group of graft chains were completely changed to the form $-\text{SO}_3\text{K}$ and $-\text{PO}_3\text{K}$, respectively. As current is supplied, K^+ ions in the A cell go through the membrane to the B cell (in Scheme 2). Fig. 7 shows the specific electrical resistance of sulfonated and phosphonated PE-g-GMA (dg=75%) as a function of the content, respectively. The specific electrical resistance decreased with an increase in the sulfonic acid and phosphonic acid content. This



Scheme 2. Apparatus for the electrical resistance and transport number measurement to ion-exchange membrane.

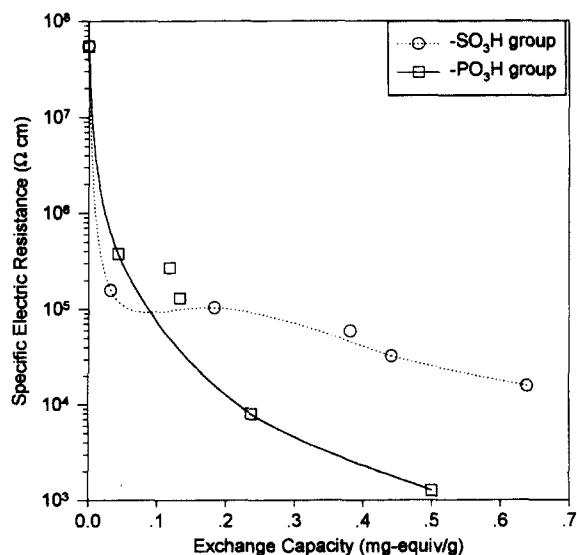


Fig. 7. Specific electric resistance of PE-g-GMA (dg=75%).

Table 3. Electrical characteristics of ion-exchange membrane modified with $-\text{SO}_3\text{H}$ and $-\text{PO}_3\text{H}$ group^{a)}

Properties	Phosphonic acid groups	Sulfonic acid groups
Electrical resistance (Ωcm)	5.0	10.2
Transport number	0.97	0.98
Ion-exchange capacity (mmol/g)	2.53	2.39
Water content (g/g) ^{b)}	0.40	0.38

^{a)} Degree of grafting (%)=150%.

^{b)} g $\text{H}_2\text{O}/\text{gK}^+$ form dry ion-exchange membrane.

result may indicate that the ion transfer depends on the ion-exchange capacity.

Table 3 shows the electrical properties of phosphonic and sulfonic cation exchange membranes. Both membranes had a similar ion-exchange capacity and similar transport number. However, the electrical resistance of the phosphonic acid membrane was lower compared with the sulfonic acid membrane. The electrical resistance difference of the phosphonic acid membrane relative to the sulfonic acid membrane might be due to the strong acidic exchange groups and the incomplete introduction of phosphonic acid groups into the PE membrane.

CONCLUSIONS

Ion-exchange membranes modified with the sulfonic acid ($-\text{SO}_3\text{H}$) and phosphonic acid ($-\text{PO}_3\text{H}$) group were prepared by radiation-induced grafting of glycidyl methacrylate (GMA) onto polyethylene (PE) films and subsequent sulfonation and phosphonation of graft poly(GMA). From the results, the conclusions were as follows:

- (1) The surface area, thickness, and volume of grafted film increased with increasing grafting yield.
- (2) Electrical resistance of phosphonated GMA-grafted PE membrane group was lower than that of sulfonated GMA-grafted PE membrane.
- (3) Transport number of phosphonated and sulfonated GMA-grafted PE membrane was about ca. 0.97-0.98.

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