

**Preparation and Electrochemical Properties of Polyethylene Membrane Modified with the Sulfonic Acid Groups for Battery Separator**

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*Abstract*

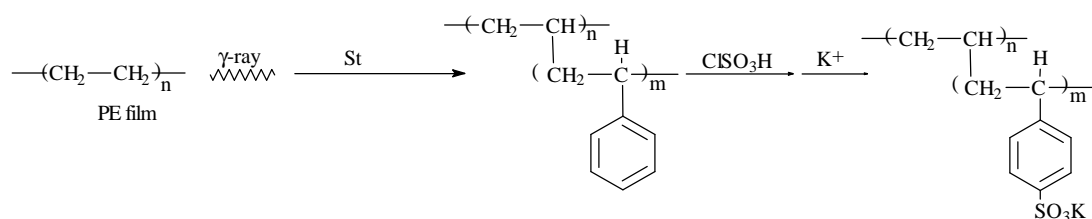
*Ion-exchange membrane modified with the sulfonic acid group for battery separator was prepared by radiation-induced grafting of styrene (St) onto polyethylene (PE) film and subsequent sulfonation of poly(St) graft chains.*

*The surface area, thickness, and volume of grafted film increased with increase in grafting yield. The water uptake and KOH diffusion flux of ion-exchange membrane increased with increase in the sulfonic acid content. Electrical resistance of ion-exchange membrane modified with the sulfonic acid group decreased with increase in the sulfonic acid content. The transport number ( $t_+$ ) of  $K^+$  in the sulfonated membrane was in the range of 0.91 – 0.96.*

**I. Introduction**

Radiation-induced grafting is a good method for introduction of functional groups into different polymer materials by specially selected monomer. A number of papers were published on radiation graft copolymerization of polar monomers onto hydrophobic polymer matrix to obtain hydrophilic property for versatile applications.<sup>1-4</sup> Among them, ion-exchange membrane was used as the adsorption of metal ions,<sup>5</sup> water desalination,<sup>6</sup> separators in alkaline batteries,<sup>7</sup> etc.<sup>8</sup>

Scheme I. Preparation of Cation-Exchange Membrane for Battery Separator



In a previous study,<sup>9</sup> the grafting of styrene onto PE hollow fiber membrane was carried out by the pre-irradiation grafting technique. The effects of the reaction time, the reaction

temperature, and additives such as  $H_2SO_4$ , and divinylbenzene on the grafting reaction were studied. From the studies, it was found that the additives such as ferrous salts, sulfuric acid, and divinylbenzene could enhance the grafting yield in radiation grafting process. In a previous paper,<sup>10</sup> we also prepared ion-exchange membrane modified with carboxylic acid group by radiation-induced grafting of acrylic acid (AA) and methacrylic acid (MA) onto a PE film. The surface area, thickness, volume, water uptake, and ion-exchange capacity, specific electric resistance, and electrolyte flux were evaluated after PE was grafted with AA and MA. It was found that KOH diffusion flux of AA-grafted PE membrane and MA-grafted PE membrane increased with increase in the degree of grafting. AA-g-PE membrane had a higher diffusion flux than MA-g-PE membrane. Electric resistance of two cation-exchange membrane modified with AA and MA decreased rapidly with increase in the degree of grafting. However, two cation membranes had almost the same electric resistance.

In this study, ion-exchange membrane modified with the sulfonic acid group was prepared by radiation-induced grafting of styrene and its subsequent chemical modification for alkaline battery separator. The electrical resistance to the ion-exchange membrane, and electrical flux and transport number to cation-exchange membrane were examined.

## II. Experimental

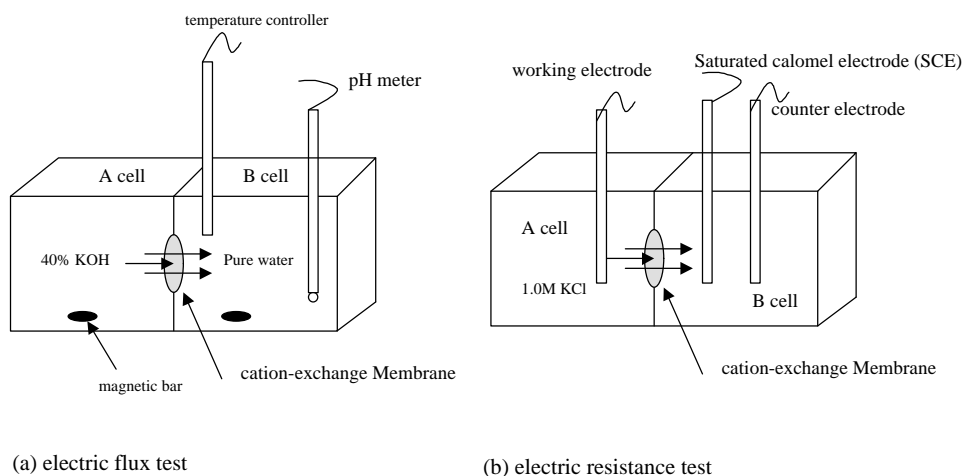
### Materials

Polyethylene (PE) film of thickness 0.03 mm was purchased from Tae-Syeng Chemistry Co. (in Korea), and washed with methanol and dried in vacuum oven at 50 °C for 8 h. Reagent-grade styrene (St, Merck) of purity 99% was used as received. The other chemicals were reagent grade, and used without further purification.

### Grafting Procedure

Scheme I shows the preparation procedure of ion-exchange membrane by the radiation

Scheme II. The apparatus for the measurement of electric flux and electric resistance of cation-exchange membrane



grafting of St onto PE film and sulfonation of poly(St) chains. The PE film was used as the base polymer for grafting polymerization. The PE film of size 4 × 5 cm was irradiated by  $\gamma$  ray from Co-60 source under atmospheric pressure and ambient temperatures, and then immediately irradiated PE film was reacted with St monomer. The unreacted monomer and homopolymers after grafting of St were removed with benzene using Soxhlet apparatus, the modified PE film obtained by grafting polymerization was dried in vacuum oven at 50 °C for 14 h. For the studies of the effects of various parameters on the grafting polymerization, 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.

### Sulfonation of St-grafted PE Film

Poly-styrene in St-grafted PE film was reacted with 5%-ClSO<sub>3</sub>H in ClCH<sub>2</sub>CH<sub>2</sub>Cl in a glass ampoule at various times and concentrations, respectively. After the sulfonation, the cation-exchange membrane was washed with the order of 99% H<sub>2</sub>SO<sub>4</sub> > 50% H<sub>2</sub>SO<sub>4</sub> > 20% H<sub>2</sub>SO<sub>4</sub> > deionized water, and was dried under reduced pressure. The -SO<sub>3</sub>H group content was determined from measurement of total ion-exchange capacity by titration. -SO<sub>3</sub>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 0.025N NaOH aqueous solution.

### Electrolyte Flux Test

Scheme II shows the experimental apparatus for measuring electrical flux and the electrical resistance. With this apparatus, the permeation from an aqueous 40% (by weight) potassium hydroxide (KOH) solution through the membrane into distilled water was monitored by measuring the pH of the solution in the receiving cell. The pH values were continuously recorded, from which the diffusion rate of the hydroxy ion-versus-time curves was calculated. The electrical flux,  $U_i$  (mol cm<sup>-3</sup> sec<sup>-1</sup>), was determined by

$$U_i = (\text{diffusion rate}) / T S \quad (2)$$

where  $S$  denoted the surface area (cm<sup>2</sup>) of the membrane.  $T$  denotes thickness (cm) of membrane.

### Electrical Resistance

The electrical resistance of -SO<sub>3</sub>H form membrane was measured in 1.0 M KCl

solution at 25 °C using an IM5-D impedance spectroscopy (ZRNER Meßtechnik Co. in Germany ) working 1000 Hz. The specific electrical resistance,  $R_{sp}$  ( $\Omega$  cm) was calculated by the next equation:

$$R_{sp} = \{[(R_{soln+membr} - R_{soln}) / T] \cdot l\} \cdot S \quad (3)$$

where  $R_{soln+membr}$  denote the electrical resistance of KCl solution in the presence of membrane, and  $R_{soln}$  denote the electrical resistance of KCl solution without membrane.

### Transport Number ( $t_+$ )

The synthesized  $-\text{SO}_3\text{H}$ -form membrane was conditioned in 0.75N KCl solution for 1 day at room temperature, and then placed in between two compartments to measure the electromotive force of chemical cell. KCl solutions of 0.5 and 1.0 N were made to flow individually through the compartments until equilibrium was reached. The membrane potential was measured at 25 °C using IM5-D impedance spectroscopy. The transport number ( $t_+$ ) of counterions in the membrane was calculated from the value of the measured potential ( $E_m$ ) by the following equation:

$$t_+ = E_m / 2E_o + 0.5 \quad (4)$$

where  $E_o$  is the theoretical potential calculated by the Nernst equation

$$E_o = RT / F \ln(C_2\gamma_1 / C_1\gamma_2) \quad (5)$$

where  $\gamma_1$  and  $\gamma_2$  are the activity coefficients of KCl at concentration  $C_1$  and  $C_2$ , respectively.

## III. Results and Discussion

Table 1, 2 shows the effects of St and  $\text{H}_2\text{SO}_4$  concentration on the grafting of St onto PE film in the presence of ferrous sulphate or Mohr's salt. Maximum grafting yield occurred in monomer concentration of 5.85M except the addition of 0.1M  $\text{H}_2\text{SO}_4$ . This indicates that important factor for grafting is the monomer concentration. As shown in Table 1, 2, with the addition of sulfuric acid and ferrous salt, the grafting yield was much enhanced. Ferrous sulphate ( $\text{FeSO}_4$ ) and Mohr's salt  $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4]$  are two of the most commonly used compounds for inhibiting the homopolymerization of vinyl monomer during grafting polymerization.<sup>11</sup> The reason for this is that, as shown by Garnett,<sup>12</sup> the ferrous ion ( $\text{Fe}^{2+}$ ) present in this compound has the high rate constant for the reaction with the hydroxyl radical,

and so it effectively mops up these radicals before they react with the monomer. In a previous work,<sup>13</sup> the influence of inhibitor concentration on the degree of grafting was examined by using FeSO<sub>4</sub> as the homopolymerization inhibitor.

Table 3 shows the effect of St concentration and reaction temperature on the grafting of St onto

Table 1. Effects of Sulfuric Acid and Monomer Concentration on the Grafting of St onto PE Film <sup>a)</sup>

St concentration (M)	Degree of grafting (%)			
	FeSO <sub>4</sub> ·7H <sub>2</sub> O <sup>b)</sup>			
	No H <sub>2</sub> SO <sub>4</sub>	0.025M H <sub>2</sub> SO <sub>4</sub>	0.05M H <sub>2</sub> SO <sub>4</sub>	0.1M H <sub>2</sub> SO <sub>4</sub>
neat	17.2	---	----	----
6.30	37.1	44.3	60.1	122.8
5.85	36.9	52.7	67.4	102.4
5.40	10.6	41.1	47.8	75.0
4.95	5.6	17.9	29.3	36.9
4.50	2.3	13.2	14.6	17.4

<sup>a)</sup> Irradiation dose 30 kGy, PE film 0.03 mm, reaction time 15 h, at 70 °C, in MeOH.

<sup>b)</sup> Concentration = 2.5 × 10<sup>-3</sup>M.

Table 2. Effects of Sulfuric Acid and Monomer Concentration on the Grafting of St onto PE Film <sup>a)</sup>

St concentration (M)	Styrene	Degree of grafting (%)			
		FeSO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·6H <sub>2</sub> O <sup>b)</sup>			
		No H <sub>2</sub> SO <sub>4</sub>	0.025M H <sub>2</sub> SO <sub>4</sub>	0.05M H <sub>2</sub> SO <sub>4</sub>	0.1M H <sub>2</sub> SO <sub>4</sub>
neat	6.5	16.7	—	—	—
6.30	9.3	35.4	43.4	58.7	123.0
5.85	7.4	38.2	47.5	64.7	120.0
5.40	3.2	10.2	40.1	47.8	74.0
4.95	1.0	6.0	15.9	29.0	40.6
4.50	~ 0	3.1	12.3	15.6	15.8

<sup>a)</sup> Irradiation dose 30 kGy, PE film 0.03 mm, reaction time 15 h, at 70 °C, in MeOH.

<sup>b)</sup> Concentration = 2.5 × 10<sup>-3</sup>M.

PE film at reaction temperature of 30, 50, 70 °C for reaction time of 15 h. The grafting yield at 70°C was high, compared to 30 °C and 50 °C. The reason for this is due to radicals formed when the peroxide caused by oxygen during irradiation in air is decomposed at the temperature of 70 °C. Therefore, a reactively higher temperature is required to obtain a high grafting yield.

Table 4 shows the effects of monomer concentration and total radiation dose on the grafting of St onto PE film. The reaction temperature was set at 70 °C for reaction time of 15 h.

Table 3. Effects of Reaction Temperature and St Concentration on the Grafting of St onto PE Film in the presence of Ferrous Salt <sup>a)</sup>

St concentration (M)	Degree of grafting (%)		
	30 °C	50 °C	70 °C
neat	~ 0	8.5	17.2
6.30	8.3	15.3	37.1
5.85	7.3	14.6	36.9
5.40	5.6	7.8	10.6
4.95	1.0	2.6	5.6
4.50	~0	0.8	2.3

<sup>a)</sup> Irradiation dose 30 kGy, PE film 0.03 mm, ferrous sulphate  $2.5 \times 10^{-3}$ M, reaction time 15 h, in MeOH.

Table 4. Effects of Irradiation Dose and Monomer Concentration on the Grafting of St onto PE Film in the presence of Fe<sup>2+</sup> <sup>a)</sup>

St concentration (M)	Degree of grafting (%)		
	20 kGy	30 kGy	40 kGy
neat	10.4	17.2	20.8
6.30	31.2	37.1	41.2
5.85	32.4	36.9	40.9
5.40	9.7	10.6	14.9
4.95	5.0	5.6	8.7
4.50	1.9	2.3	7.0

<sup>a)</sup> PE film 0.03 mm, reaction time 15 h, at 70 °C, Fe<sup>2+</sup> concentration =  $2.5 \times 10^{-3}$ M, in MeOH.

Grafting increased with increase in total radiation dose.

Fig. 1 shows the change in dimension of the polymer film with grafting. Both the thickness and the surface area of the film increased linearly with increase in the grafting yield. These increase are due to the growth of graft chains inside the polymer film. Because the graft polymerization occurs mainly in the amorphous region of the film, the growth of the graft chain

is assumed to expand the amorphous region of the film. In other words, the grafting occurs mainly at the mechanically weak part of the trunk polymer. 75% styrene-grafted PE film was dipped into a mixture of 5%  $\text{ClSO}_3\text{H}/\text{ClCH}_2\text{CH}_2\text{Cl}$  to make the cation-exchange membrane having  $-\text{SO}_3\text{H}$  group.

The water uptake (%) of sulfonated membrane (dg = 75%) as a function of the ion-exchange capacity content was examined (not shown here). The linear increase indicates that the water uptake is due to the hydrophilic acid groups of the graft chains.

Fig. 2 shows the specific electrical resistance of PE-g-St containing  $-\text{SO}_3\text{H}$  group as a function of the  $-\text{SO}_3\text{H}$  group content. The specific electrical resistance decreased with increase in the sulfonic acid content. This result may indicate that the ion transfer depends on the ion-exchange capacity.

### Acknowledgement

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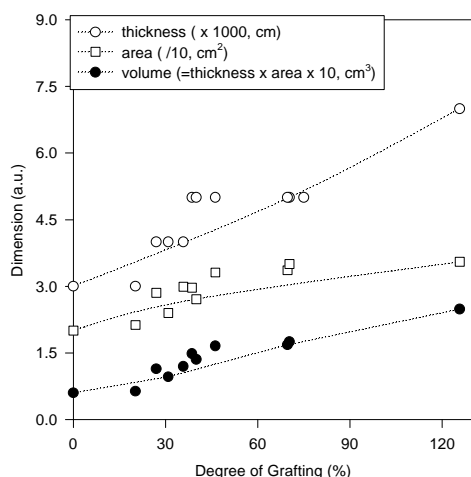


Fig. 1. Change of dimension of the St-grafted PE film.

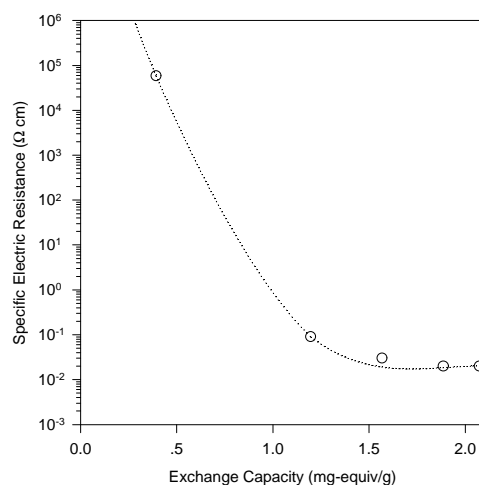


Fig. 2. Specific electric resistance of sulfonated membrane (dg=75%).

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