

일반강연 A-2

플라즈마 중합법에 의해 제조된 불균일한  
단면분포를 가진 이온교환막의 특성분석

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**Characterization of inhomogeneous IEMs prepared by  
plasma graft polymerization**

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**1. Introduction**

Morphology of membrane affects its performance [1]. For a constant amount of fixed charges, the distribution of these charges is also significant to its performance [2]. In some ionomer membranes such as Nafion, the membrane fixed charge is not randomly distributed, but occurs in clusters. Thus, the membrane solution is phase-separated, with the ion clusters, acting as inverted micelles in a polymer solvent. There has been reported that inhomogeneities in the fixed ion distribution (due to the cluster morphology) give rise to a potential with the membranewhich impedes co-ion relative to counterion transport, increasing current efficiency and the selectivity of a membrane can be improved by distributing the fixed charges nonuniformly. [3,4]. Yamaguchi et al [5] reported that membrane morphology with the plasma graft filling polymerization could be controlled by solvent-dependent activity. Varying the monomer solvent composition (water and methanol) could affect the graft polymerization rate by changing the monomer diffusivity relative to the reactivity. Using the water solvent, surface region was rich in grafted polymer compared to the middle of the film, which led to nonuniform distribution of the grafted polymer across the membrane whereas the use of mixture of water and methanol led to homogeneous membrane.

In this study, we prepare CEMs with nonuniformly distributed fixed charges by dissolving GMA in a proper composition of water and methanol and grafting it using plasma graft polymerization and sulfonating. Also, the prepared membranes are characterized in terms of the physical and electrochemical properties of the prepared membrane such as membrane electric resistance, transport number, current-voltage and surface heterogeneity, ion-exchange capacity and water swelling ratio.

## 2. Experimental

### 2.1. Materials

Porous polypropylene (PP) film was used as the substrate. The PP substrate, with a thickness of 25 $\mu\text{m}$  and a pore size of  $0.250 \times 0.075 \mu\text{m}^2$ , was supplied by Celgard Co. Ltd. Glycidal metaacrylate (GMA, Adrich) were used as a grafting monomer and/or mediator to introduce an anion-fixed moiety onto the PP film. Mixture consisting of sodium sulfite, sodium bisulfite, isopropyl alcohol and water (10/3/10/77 weight ratio), was prepared and used as a reagent to introduce sulfonic moiety onto the film. All reagents were used without further purification.

### 2.2. Membrane preparation

To remove active gases in the monomer solution, the solution was thawed and frozen repeatedly with liquid nitrogen under a vacuum of 30 mtorr. Square film of PP is treated for 30 sec by radio-frequency plasma operating at 13.65 MHz and delivering 10 W under 75 mtorr argon atmosphere using the apparatus for plasma graft polymerization shown in Fig. 2. The resulting film was immersed in the monomer solution without contacting air for predetermined time. Mixture of menthol and water was used as a solvent. The grafted films are washed in water and rinsed with dimethylformamide to remove the unreacted monomer and homopolymer, and the 40-45 °C in an oven. The amount of grafted portion of the membrane was calculated as follows

$$\text{The degree (dg) of grafting} = [(W_1 - W_0) / W_0]100 \quad (1)$$

where  $W_0$  is the weight of the polymer film before grafting and  $W_1$  is the weight of after the grafted polymer. Then, GMA-grafted PP film was immersed in the mixture consisting of sodium sulfite, sodium bisulfite,

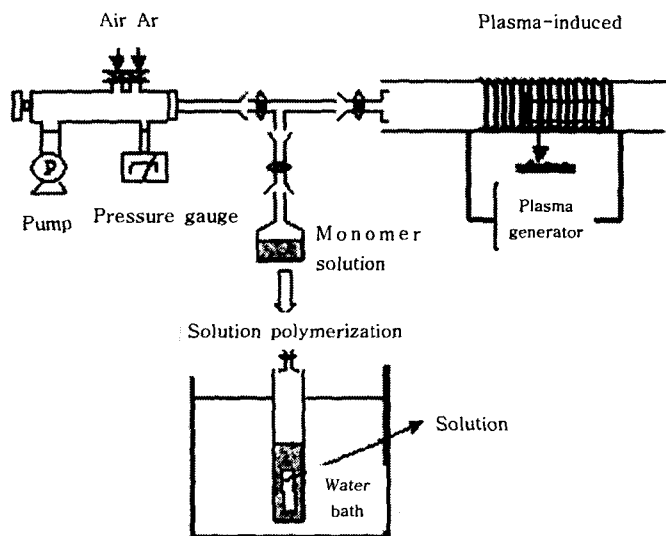


Fig. 1. Apparatus for plasma graft polymerization

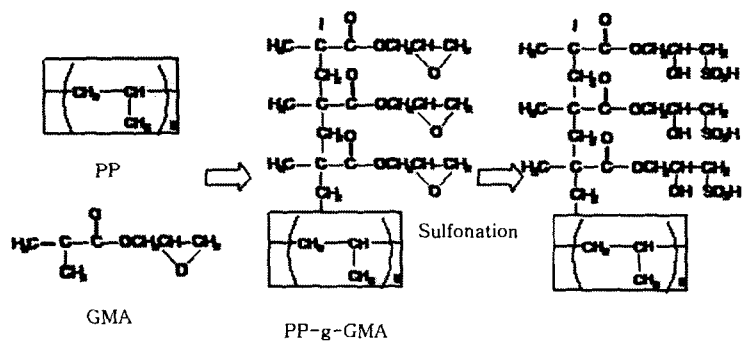


Fig. 2. Apparatus for plasma graft polymerization

### 3. Results and Discussion

isopropyl alcohol and water for predetermined time to introduce sulfonic moiety. The preparation scheme of these CEMs was summarized in Fig. 3.

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### **References**

- [1] Larter, R., *J. Membr. Sci.*, 28 (1986) 165
- [2] Jyh-Ping Hsu and Kuo-Chiang Ting, Current efficiency of an ion-selective membrane: Effect of fixed charge distribution, *J. Electrochem. Soc.* 145 (1998) 1088-1092
- [3] H. Reiss and I. C. Bassignana, Critique of the mechanism of superselectivity in ion exchange membranes, *J. Membr. Sci.*, 11 (1982) 219-229
- [4] C. Servey and H. Reiss, Ion transport in inhomogeneous ion exchange membrane, *J. Membr. Sci.* 23 (1985) 11-27
- [5] T. Yamaguchi, S. Nakao and S. Kimura, Evidence and mechanisms of filling polymerization by plasma-induced polymerization, *J. Appl. Polym. Sci.*, 34, 1203-1208 (1996)