

**플라즈마 중합법에 의해 제조된 carboxylic,
phosphonic, sulfonic 그룹 양이온교환막의
전기화학적 특성**

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**Electrochemical characteristics of carboxylic, phosphonic,
sulfonic acid cation-exchange membrane prepared by
plasma-induced graft polymerization**

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1. Introduction

The basic nature of ion-exchange membrane (IEM) on ion-selective performance includes, the type of fixed ionic moiety (cationic and anionic), the amount of fixed charges, the distribution of fixed charges and morphological shape (compactness caused by crosslinking reaction). Among these factors, a type of a fixed ionic moiety in an IEM is the most important parameter to determine its performance- permselectivity and electric resistance depending on its application. Carboxylic ($-\text{COO}^-$), phosphonic ($-\text{PO}(\text{OH})\text{O}^-$ or $\text{PO}(\text{O}^-)_2$) and sulfonic groups ($-\text{SO}_3^-$) are common as fixed anionic moieties, which utilized as an ionic exchange site in a cation-exchange membrane (CEM) [1]. On the transport mechanism, comparison of sulfonic and phosphonic moieties has been investigated [2-3]. However, little has been reported on the electrochemical comparison of various anionic moieties *i.e.* carboxylic, phosphonic and sulfonic groups.

The purpose of this study is to systematically investigate electrochemical characteristics of CEMs comprising various anionic moieties, and to provide the information for membrane design to exhibit higher permselectivity. Plasma-induced graft polymerization (PIGP) is an attractive method to modify a desired function onto polymeric

materials as well as to easily control their morphology [4-5] In this study, also, carboxylic, phosphonic and sulfonic CEMs were prepared using PIGP. Membranes prepared were characterized and compared in terms of electrochemical properties, i.e. ion exchange capacity (IEC), transport number (T_n), membrane electrical resistance (MER), and chronopotentiometry.

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. Acrylic acid (AA, ACROS) and glycidal metaacrylate (GMA, Adrich) were used as a grafting monomer and/or mediator to introduce an anion-fixed moiety onto the PP film, with purification by inhibitor-removal column. Phosphonic acid was used as the reagent to introduce phosphonic moiety onto GMA-grafted PP. 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 Two weight percent GMA and 3wt % AA aqueous solutions were prepared, respectively. 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 ($7 \times 7\text{ cm}^2$) of PP was treated for 60 sec by radio-frequency plasma operating at 13.65 MHz and delivering 10 W under 75 mtorr argon atmosphere. The resulting film was immersed in the monomer solution without contacting air for predetermined time at 60. C The grafted films were washed in water and rinsed with methanol/acetone/water solution 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

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

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 85 wt% phosphoric acid for 24 h at 80. C to introduce phosphonic moiety on to the film. and in

sulfonic mixture for 24h at 80 °C to introduce sulfonic moiety.

2.3 Electrochemical characterization Membrane properties were evaluated according to pervious study [6].

3. Results and Discussion

Electrochemical properties of the prepared membranes are listed in Table 1. It was expected that the water content may decrease as a order of phosphonic CEM > sulfonic CEM > carboxylic CEM at a similar IEC because, with respect to hydrogen bond implying water-uptake possibility, the number of hydrogen bonding sites in phosphonic acid is 8, that in sulfonic acid 7 and that carboxylic acid 5, respectively. As expected, the result showed that the water content decreased as a order of phosphonic CEM > sulfonic CEM > carboxylic CEM. Also, it implies that ion channel size decreases in the order of phosphonic CEM > sulfonic CEM > carboxylic CEM. However, the change in MER was not observed thank to the thickness of the prepared membranes. Regarding the transport number, carboxylic CEM (0.88) was lower than other CEM indicating that Na⁺ affinity with the carboxylic CEM reduced more than that with phosphonic CEM and sulfonic CEM. Meanwhile, Choi et, al. calculated the fraction of conducting region (ϵ) by using chronopotentiometry in order to evaluate the surface heterogeneity of the commercial membrane. They reported that the longer transition time (τ), which τ is proportional to ϵ^2 , is due to the increase of membrane homogeneity. However, comparison of various ionic charge-fixed IEM cannot be carried out because their evaluation is limited to the same ionic charge-fixed IEM. Figure 1 shows the chronopotentiometric curves of carboxylic CEM with various IEC. Transition time, τ , increased with increasing IEC because increasing ion-exchangeable sites required longer time in the depletion of counter-ions. It can be interpreted that increasing IEC leads to the increase of surface homogeneity. Figure 2 shows the chronopotentiometric curves of carboxylic CEM, phosphonic CEM and sulfonic CEM at the constant IEC. The transition time(τ) of carboxylic CEM was longer than that of other CEMs at a nearly same IEC, indicating that the depletion of counter-ions (Na⁺) in carboxylic CEM required the longer time than that in other CEMs. Also, it is thought

that the affinity of Na⁺ with the carboxylic CEM may be lower than those phosphonic and sulfonic CEMs.

Table 1. Membrane properties

Properties	-COOH	-PO ₃ H ₂	-SO ₃ H
Water content	0.75	1.37	1.28
IEC (meq.g ⁻¹)	2.82	2.87	2.82
MER (Ωcm^2)	0.55	0.58	0.62
Transition time(τ) (s)	25.0	12.1	14.6
Transport number	0.88	0.96	0.95

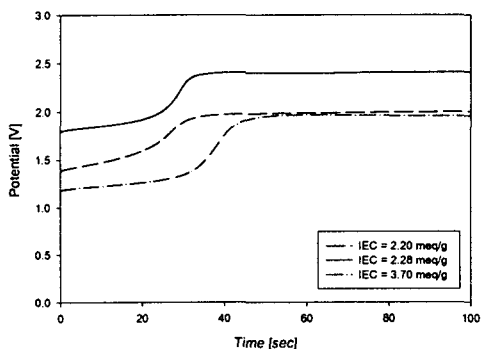


Fig. 1. Chronopotentiometry curves vs various IECs of carboxylic CEM (0.025 mol dm⁻³ NaCl, at 44.6 A/m², at 25. °C)

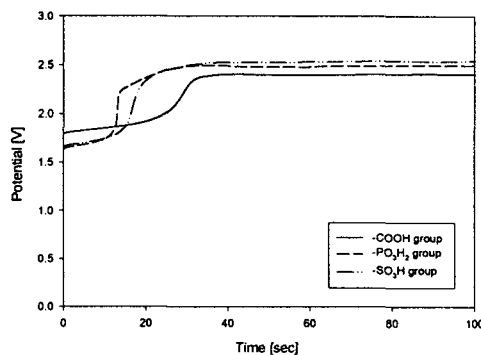


Fig. 2. Chronopotentiometry curves vs different functional group of IEM (0.025 mol dm⁻³ NaCl, at 44.6 A/m², at 25. °C)

Acknowledgement

This work was supported by the National Research Laboratory (NRL) Program of Korea Institute of Science and Technology Evaluation and Planning (Project No. 2000-N-NL-01-C-185)

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