

Synthesis of Cation-Exchange Membrane by the Monomer Sorption

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ABSTRACT

LDPE/polystyrene cation exchange membranes were prepared through a monomer-sorption method and UV radiation polymerization. The reaction behaviors in the preparation were investigated. The membranes prepared were characterized in terms of physical and electrochemical properties. The membranes exhibited reasonable properties for an ion-exchange membrane with weight gain (W_r) of above 0.3, electrical resistance of below $1.0 \Omega \text{ cm}^2$ and ion-exchange capacity of 1.8 meq/g-dry membrane. DSC studies and FE-SEM image revealed the formation of a homogeneous membrane. Both the current-voltage and the chronopotentiometric curves of the membranes indicated that LDPE/polystyrene membranes can be properly used at a high current density, and the surface homogeneity of cation-exchange sites in the membrane was comparable to that in a commercial membrane.

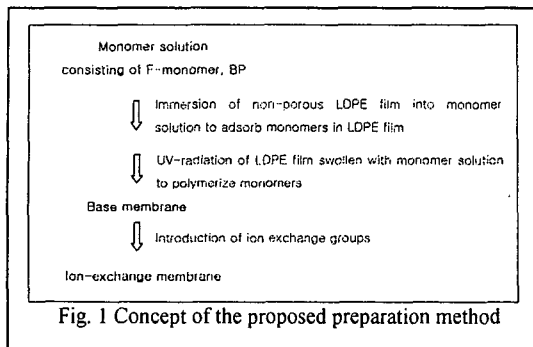
INTRODUCTION

With the advancement of electrochemically driven membrane process, a number of studies on syntheses of high performance ion-exchange membranes have progressed. To date, styrene (St)-divinylbenzene (DVB) copolymer has been particularly preferred as a basic material in the preparation of cation-exchange membranes because of its good workability and mechanical strength [1]. The membrane preparations using the copolymer have been practiced by various methods. Especially, the paste method has been popularly applied to the preparation of ion-exchange membranes. However, the paste method is somewhat complicated because the polyvinylchloride (PVC) powder and a PVC cloth are used during the preparation process, resulting in increased processing cost. To overcome the drawbacks, we studied a semi-interpenetrating polymer network (IPN) method for cation-exchange membrane by absorbing monomer solution into supporting material [2][3]. For further improvement of the membrane synthesis, photo-initiated polymerization was considered.

This study proposes a preparation method for ion-exchange membranes having higher permselectivity and homogeneity even without a chemical crosslinker. The concept of the proposed method is as follows: A non-porous supporting film was swollen with the monomers and UV-photoinitiator. When UV-beam was irradiated, the monomers could be polymerized and be grafted on polymer chain of film. As a result, the various networks could be formed and contribute to higher permselectivity and more homogeneity in the base membrane. The following sulfonation step introduced cation-exchangeable sites to the base membrane. The physical and electrochemical properties of the membranes were characterized for use in electro-driven membrane processes.

RESULTS AND DISCUSSION

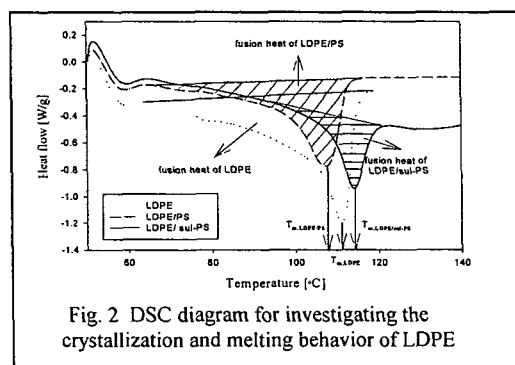
Membranes with a thickness of about 70 μm were prepared. These showed reasonable flexibility and strength (e.g. tensile strength at break, 9 MPa; elongation at break, 67%). Fig. 1 summarizes the preparation procedure.



The FT-IR/ATR spectra showed that the cation exchange membrane was successfully prepared according to the proposed method. In the base membrane (LDPE/PS), the absorption band assigned to the aromatic group was observed at 1600 and 1490 cm^{-1} . This indicates that styrene monomers were well absorbed to the non-porous LDPE film. In the sulfonated membrane (LDPE/sul-PS), the absorption band assigned to

sulfonic acid groups were observed at 1123 and 1003 cm^{-1} , and the spectra for S=O stretching vibration was observed at 1300–1160 cm^{-1} . The absorption band of aromatic groups was hidden due to strong intensity of sulfonic groups. The result indicates that the sulfonic group was introduced into the base membrane.

The polymerization ratio (W_p) in the PE film increased linearly with the increasing UV-radiation time and its polymerization rate was about 10.25 $\text{mg g}^{-1} \text{min}^{-1}$, indicating that the preparation method was a living polymerization as reported by H. Ma et. al.'s study [4]. Since the LDPE/PS membrane was synthesized by homo-polymerization and grafting-polymerization, the reactions could be described by grafting polymerization and homo-polymerization. The experiment showed that the ratio of grafting polymer to homopolymer was nearly constant during the reaction time.



The DSC diagram is presented in Fig. 2 for investigation of the crystallization and melting behavior of LDPE, LDPE/PS and LDPE/sul-PS. The melting temperature (T_m) of LDPE/sul-PS film was higher than that of LDPE film while T_m of LDPE/PS was lower than that of the LDPE film. The fusion energy (ΔH_f) was in the increasing order of ΔH_f ; LDPE/sul-PS < ΔH_f ; LDPE/PS < ΔH_f ; LDPE. This result can be explained by the diffusion of styrene monomer to crystalline of LDPE. Such phenomena caused to destroy the crystalline of LDPE and contribute to

grafting styrene monomers in the crystal region, implying that styrene was homogeneous in the LDPE matrix [5].

Further, to investigate the morphological behavior of the membranes as a function of the UV-radiation time, melting temperature (T_m) and crystallinity were attained from the DSC study. T_m and crystallinity for LDPE/PS decreased with the increasing UV-radiation time because styrene monomers were gradually grafted even in crystallites of LDPE. This led to destruction of crystallites in LDPE film with the increasing UV-radiation time. T_m of LDPE/sul-PS at 20 min decreased compared to that of LDPE. However, T_m of LDPE/sul-PS increased slightly with the increasing UV-radiation time, because the introduction of ion bond into LDPE/PS contributed to the increase in T_m . The crystallinity of LDPE/sul-PS decreased because the introduction of sulfonic groups resulted in volume expansion between grafted polymers.

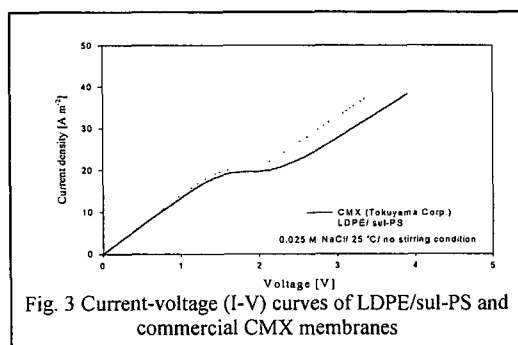
As UV-radiation time increased the polymerization ratio (W_r) and the content of PS increased. The IEC also increased with the increasing W_r , because more PS was introduced. The result agreed well with the general trend that increasing IEC leads to decreasing MER [6].

Table 1 shows the basic properties of the membrane prepared in this study and commercial membrane, CMX. The LDPE/sul-PS membrane ($W_r = 0.49$) exhibited the ion exchange capacity, electric resistance and transport number, comparable to those of commercial membranes.

Membrane	LDPE/ sul-PS	CMX (Tokuyama co.)
IEC [meq. /g-dry memb.]	1.60	1.80
MER [ohm cm ²]	0.96	3.10
Transport number (for Na ⁺) [-]	0.99	0.98

Table 1 Comparison of the present membrane with CMX membrane on the general properties

Fig. 3 shows the I-V characteristics of the membranes prepared in this study. The slopes in the I-V curves give useful information on the ion transport under and over limiting current density (LCD). Choi *et al.* analyzed the I-V curves of cation-exchange membranes in various electrolyte solutions. They suggested that the R_{3rd}/R_{1st} (the resistance ratio) and ΔV (the plateau length) values of I-V curves result from the electroconvective effects over LCD. Namely, the lower R_{3rd}/R_{1st} and the shorter ΔV indicate the more active electroconvective effect. Since these parameters are directly related to the power consumption in operation at a current density over LCD, they are critical electrochemical properties of ion-exchange membrane [7]. The membranes prepared exhibited lower R_{3rd}/R_{1st} and ΔV values than the commercial membranes. This result implies



that the present membranes can be properly used at a high current density. In addition, the superficial LCD values of the present membranes were slightly higher than those of the commercial membranes, due to the higher portion of non-conducting area in the commercial membranes. The results illustrate that the distribution of cation-exchange sites of the membrane prepared in this study was more homogenous than a commercial membrane prepared by a paste method.

From the chronopotentiometric study, the fraction of conductivity region (ϵ) was calculated. The ϵ values of LDPE/sul-PS membrane were slightly higher than that of CMX membrane. In the case of heterogeneous membrane, much lower ϵ value was observed than those of other membranes. From the results, the ion-exchangeable groups were found to be homogeneously introduced on the surface of the LDPE/PS membrane prepared in this study.

CONCLUSIONS

LDPE/sul-PS cation exchange membranes were prepared via the combination of the monomer sorption method and UV-radiation polymerization. The prepared membranes were characterized in terms of physical and electrochemical properties. The membranes exhibited reasonable mechanical properties for an ion-exchange membrane. DSC studies and FE-SEM image revealed the formation of a homogeneous membrane. Electrochemical characterization of the resulting membrane showed a low membrane electrical resistance ($< 1 \Omega \text{ cm}^2$) and a reasonable ion-exchange capacity (about 1.8 meq/ g-dry mem.). The I-V curves of the membrane indicate that the LDPE/sul-PS membrane can be properly used at a high current

density. This study demonstrates that the combination of monomer sorption method and UV-radiation polymerization enabled to prepare a homogenous ion exchange membrane with high compatibility between LDPE and polystyrene.

REFERENCES

1. Y. Mizutani, Structure of ion-exchange membranes, *J. Membr. Sci.* 49 (1990) 121.
2. Y.-J. Choi, M.-S. Kang and S.-H. Moon, A new preparation method for cation-exchange membrane using monomer sorption into reinforcing materials, *Desalination* 146 (2002) 287.
3. Y.-J. Choi, M.-S. Kang, S.-H. Moon, Characterization of Semi-IPN Polystyrene Cation-Exchange Membranes, *J. Appl. Polym. Chem.*, 88, (2003) 1488.
4. H. Ma, R.H. Davis and C.N. Bowman, A novel sequential photoinduced living graft polymerization, *Macromolecules* 33 (2000) 331.
5. S. Hietala, M. Paronen and S. Holmberg, Phase separation and crystallinity in proton conducting membranes of styrene grafted and sulfonated poly(vinylidene fluoride), *J. Polym. Sci.: Part A: Polym. Chem.* 37 (1999) 1741.
6. F. Helfferich, Ion exchange, Dover publication Inc., New York, 1995.
7. J.-H. Choi, H.-J. Lee and S.-H. Moon, Effects of electrolytes on the transport phenomena in a cation-exchange membrane, *J. Coll. & Interf. Sci.* 238 (2001) 188.