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Synthesis of Ion-Exchange Membranes by Radiation Graft Polymerization

Hisashi Ohtaka[1], Kazuya Ohkubo[1], Mitsuhiro Takeda[1], Yoshinobu Tanaka[1], Takanobu Sugo[2] and Isao Ishigaki[2]

[1]*Sea Water Science Research Laboratory, Japan Tobacco Inc., Kanagawa, Japan*
[2]*Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Gunma, Japan*

ABSTRACT

In Japan, table salt has been manufactured by ion-exchange membrane electrodialysis. Synthesis of ion-exchange membranes is one of the most important components for electrodialysis. A problem encountered in the manufacturing process of commercial membranes is that it consists of so many steps that a high membrane manufacturing costs are incurred.

In order to simplify the membrane manufacturing process of the membranes, we synthesized the ion-exchange membranes by pre-irradiation graft polymerization. As a result of concentrating seawater using these membranes, the current efficiency was lower compared with that of commercial membranes. This is supposedly because the transport number of the synthesized membranes is low. In addition, the solute diffusion coefficient, the electro-osmosis coefficient and the concentration osmosis coefficient of the synthesized membrane were recognized to be higher with increasing degree of grafting.

In order to improve the properties of membranes and the seawater concentration performance to bring them into line with the commercial ones, it was concluded that the concentration of dissociating groups in the synthesized membranes should be raised by increasing both the ion-exchange capacity and the degree of cross-linking.

INTRODUCTION

In Japan, about 1.4 Mt of table salt have been manufactured annually by ion-exchange membrane electrodialysis. The synthesis of ion-exchange membranes is one of the most important components of electrodialysis. The manufacturing process of commercial membranes is as follows. A monomer solution is prepared by mixing styrene, divinylbenzene, polymerization initiators and plasticizers, etc. Base membranes are produced by coating and polymerizing the mixed solution on a network of polyvinylchloride thread. Ion-exchange membranes are obtained by introducing dissociating groups into the base membranes (Mineki et al., 1973). A problem encountered in this process is that it consists of so many steps that it incurs high membrane manufacturing costs of the membranes.

In order to try to simplify the base membrane manufacturing process, we have synthesized ion-exchange membranes by irradiation graft polymerization. We have also measured the properties of membranes and have concentrated seawater using these membranes. Based on these experimental results, we discuss methods for improving the properties of membranes and the seawater concentration performance.

EXPERIMENTAL

Synthesis of membranes

The pre-irradiation method was used for graft polymerization. Figure 1 shows this process. Firstly, a polyethylene film of 100 μm thickness was irradiated with 200 kGy electron beams under nitrogen gas and free radicals were formed in the film. As shown in Fig. 2, the irradiated film was put into a glass ampoule and this was evacuated. Then, a solution (a mixed solution of styrene or chloromethylstyrene and swelling solution, benzene) which had been deaerated by nitrogen gas was introduced into the ampoule and graft polymerization was carried out at 50°C. After the polymerization, the film was washed repeatedly with benzene and methanol and was dried under a vacuum. The degree of grafting is determined by the following equation.

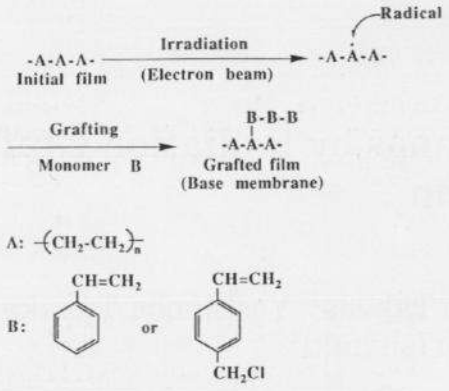

Fig. 1. Graft polymerization process by pre-irradiation.

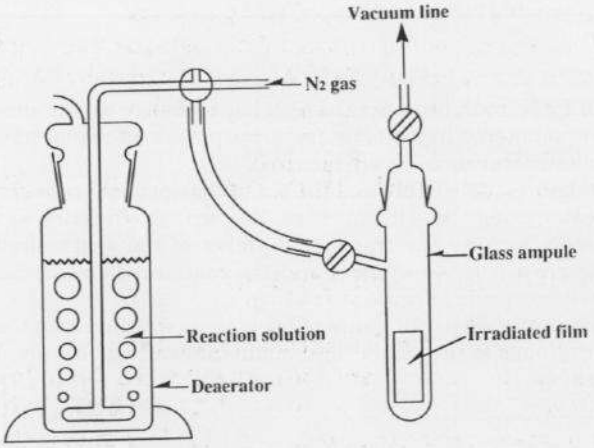

Fig. 2. Graft polymerization apparatus.

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

where W_g is the weight of the grafted film, and W_i is the weight of the initial (polyethylene) film.

The styrene grafted film was put into a 10% chlorosulfonic acid solution of dichloromethane at 0–2°C for 1 h. After sulfonation, a cation-exchange membrane was obtained by washing completely with methanol and distilled water.

The chloromethylstyrene grafted film was put into a 10% trimethylamine aqueous solution at 50°C for 1 h. After quarternalization, an anion-exchange membrane was obtained by washing repeatedly with distilled water.

Concentration of seawater

Eight desalinating chambers (6.5 mm thick) and 7 concentrating chambers (1.5 mm thick) were arranged through synthesized cation and anion-exchange membranes (effective membrane area, 8 cm^2) in a small electrodialyzer as illustrated schematically in Fig. 3. The seawater at 25°C was supplied to the electrodialyzer and an electric current was passed through the electrodes. After the electrolyte concentration of the concentrated solution flowing out from the electrodialyzer was found to be constant, the volume was measured and the ionic components were analyzed. The electrodialytic experiment was repeated at different current densities.

Transport number, solute diffusion coefficient, electro-osmosis coefficient and concentration osmosis coefficient

The transport of ionic electrolytes, m, can be expressed by equation (2) in which λi and $\mu(C_2–C_1)$ correspond to electric migration and electrolyte diffusion, respectively. The transport of electrolyte solution, q, may be expressed as equation (3) in which ϕi and $\varrho(C_2–C_1)$ correspond to electro-osmosis and concentration osmosis, respectively.

$$m = \lambda i - \mu(C_2–C_1) \quad (2)$$

$$q = \phi i + \varrho(C_2–C_1) \quad (3)$$

where m is the ionic migration per unit of time and membrane area (eq/cm^2·h); q is the solution migration per unit of time and membrane area (cm^3/cm^2·h); i is the current density (A/cm^2); C_i is the ion concentration in desalting chamber (eq/cm^3); C_2 is the ion concentration in concentration chamber (eq/cm^3); λ is a parameter for transport number (eq/A·h); μ is the solute diffusion coefficient (cm/h); ϕ is a parameter for the electro-osmosis coefficient (cm^3/A·h); ϱ is the concentration osmosis coefficient (cm^4/eq·h).

Plotting m/i or q/i to $(C_2–C_1)/i$, we obtain straight lines. From the intercepts and the gradients of the lines, we obtain λ, μ, ϕ and ϱ (Tanaka, 1985).

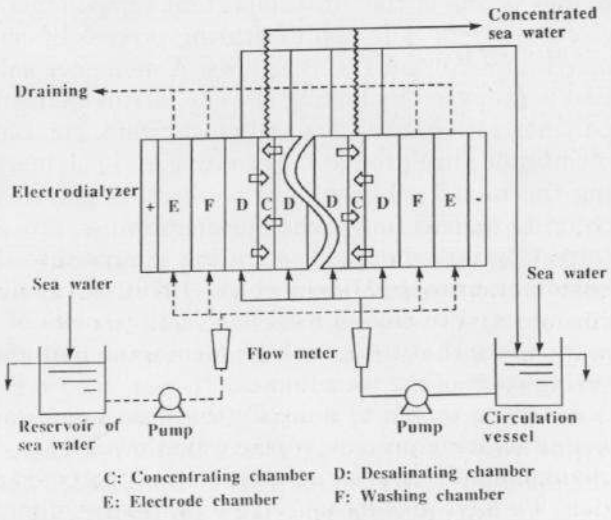

Fig. 3. Electrodialyzer for concentration of seawater.

TABLE 1
Properties of membranes

		Degree of grafting (%)	Thickness of membrane (mm)	Electric resistance ($\Omega \cdot cm^2$)	Ion-exchange capacity (meq/g)	Water content ($g \cdot H_2O/g$)	Concentration of dissociating groups ($meq/g \cdot H_2O$)
Case 1	Cation	30.4	0.13	1.75	1.07	32.7	3.28
	Anion	26.9	0.14	3.02	1.34	13.7	9.83
Case 2	Cation	42.8	0.13	1.19	2.40	51.7	4.64
	Anion	69.5	0.14	0.91	2.18	38.9	5.60
Commercial membrane	Cation	–	0.12	2.05	1.55	25.0	6.20
	Anion	–	0.14	1.90	1.85	24.5	7.55

Electric resistance

Ion-exchange membranes were equilibrated in a 0.5 N NaCl solution at 25°C and the electric resistance was measured applying AC at 1 kHz (Senoh and Tanaka, 1984).

Ion-exchange capacity

The cation-exchange capacity was measured as follows. Sulfonate groups were changed to H groups by putting the cation-exchange membrane into 1 N HCl. The membrane was thoroughly washed with distilled water and immersed in 2 N NaCl several times in order to change the sulfonic acid groups into Na groups. H^+ ions isolated in the 2 N NaCl were titrated by 0.1 N NaOH.

The anion-exchange capacity was measured as follows. Ammonium groups were changed to Cl groups by putting the anion membrane into 1 N NaCl. The membrane was thoroughly washed with distilled water and immersed in 1 N $NaNO_3$ several times in order to change the ammonium groups into NO_3 types. Cl^- ions isolated in the 1 N $NaNO_3$ were titrated by 0.1 N $AgNO_3$.

The ion-exchange capacity was obtained as milliequivalent of ionic groups per gram of dry membrane [meq/g] (Senoh and Tanaka, 1984).

Water content

An Na-type cation or a Cl-type anion-exchange membrane was immersed in 0.5 N NaCl until equilibrium conditions were attained and the weight of wet membrane was measured. The membranes were then dried under vacuum at 50°C until the weight was constant. Then, the weight of the dried membrane was measured. Water content per gram of dried membrane ($g \cdot H_2O/g \times 100 = \%$) was determined from the weight difference between the wet and the dry membranes (Senoh and Tanaka, 1984).

Concentration of dissociating groups

Concentration of dissociating groups per unit water content ($meq/g \cdot H_2O$) was determined by using equation (4) (Senoh and Tanaka, 1984).

$$\text{Concentration of dissociating groups} = (\text{Ion exchange capacity/water content}) \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Properties of synthesized membranes

In these experiment, we synthesized both low grafting degree membranes (Case 1) and high grafting degree membranes (Case 2). Table 1 shows the grafting degree, the membrane thickness, the electric resistance, the ion-exchange capacity, the dissociating group concentration and the water content of synthesized membranes and compares them with commercially available membranes.

Seawater concentration performance

The relationship between current density and total ion current efficiency are shown is Fig. 4. The current efficiency of synthesized membranes can be

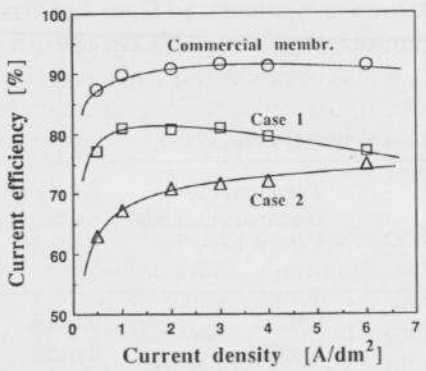

Fig. 4. Relationship between current density and total ion current efficiency.

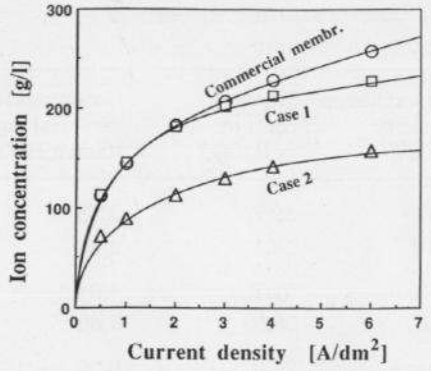

Fig. 5. Relationship between current density and ion concentration.

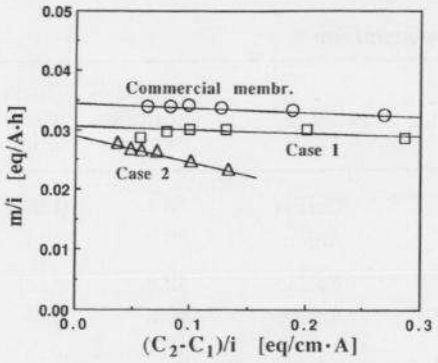

Fig. 6. m/i vs. $(C_2–C_1)/i$ plot.

seen to be low, particularly, when degree of grafting is high. The current efficiency of Case 2 was less than that of Case 1. However, the current efficiency of either Case 1 or Case 2 never exceeded that of the commercially available membranes.

Figure 5 shows the ion concentration of concentrated seawater vs. current density plot. No significant difference was found between Case 1 and the commercial membrane for less current density them 2 (A/dm^2). The concentration for Case 2 was less than that for Case 1 and the commercial membrane.

Transport number, solute diffusion coefficient, electro-osmosis coefficient and concentration osmosis coefficient

Figures 6 and 7 show the plot of m/i vs. $(C_2–C_1)/i$ and q/i vs. $(C_2–C_1)/i$ respectively. Table 2 shows the values of λ, μ, ϕ and ϱ that were obtained from Figs. 6 and 7. The average transport numbers, $\bar{t}$, of cation and anion membranes were calculated from λ.

(a) Transport number λ

Values of λ of the synthesized membranes were lower compared with the value of the commercial one. The average transport number of cation and anion membranes, $\bar{t}$ calculated from λ of Case 1 was 0.92 and that of Case 2 was 0.89. On the other hand,

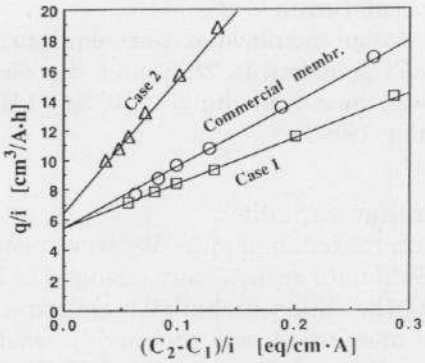

Fig. 7. q/i vs. $(C_2–C_1)/i$ plot.

$\bar{t}$ of the commercial membrane was 0.97. Current efficiency deterioration of the synthesized membranes was thought to be caused by the lowering of the transport number.

(b) Solute diffusion coefficient μ

The difference between the values of μ of Case 1 and the commercial membrane was insignificant. However, the value of μ of Case 2 was greater than the others. This is presumably another reason for the extreme current efficiency deterioration of Case 2. The increase of solute diffusion coefficient is

TABLE 2

Characteristics of membranes

	Parameter for transport number λ (eq/A·h)	Solute diffusion coefficient μ (cm/h)	Parameter for electro-osmosis coefficient ϕ (cm^3/A·h)	Concentration osmosis coefficient ϱ (cm^4/eq·h)	Average transport number $\bar{t} = (\bar{t}_K+\bar{t}_A)/2$
Case 1	0.0311	0.0076	5.37	30.9	0.92
Case 2	0.0293	0.0422	6.39	93.0	0.89
Commercial membrane	0.0347	0.0074	5.18	43.6	0.97

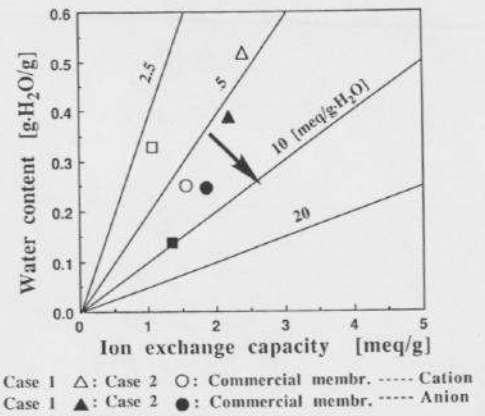

Fig. 8. Relationship between ion exchange capacity and water content.

thought to be brought about by the expansion of the matrix in a polyethylene film because of the increase of degree of grafting.

(c) Electro-osmosis coefficient ϕ

There was no significant difference in ϕ between Case 1 and the commercial membrane. The value of ϕ of Case 2 was higher than that of the commercial membrane because of the expansion of the matrix in the polyethylene film.

(d) Concentration osmosis coefficient ϱ

The ϱ of Case 1 was lower compared with that of the commercial membrane. This is because the water osmosis in Case 1 was less than that in the commercial membrane. Further, because of the smaller figure for ϱ of Case 1, the ion concentration of the concentrated seawater for Case 1 did not decrease compared with that for the commercial membrane, despite the fact that the transport number of Case 1 is smaller than that of the commercial membrane. In the case of Case 2, however, the value of ϱ was larger but the transport number was smaller compared with the values of the commercial membrane. For this reason, the ion concentration of the concentrated seawater for Case 2 decreased.

Ion-exchange capacity, water content and concentration of dissociating groups

Figure 8 shows the relationship between ion-exchange capacity and water content. The straight lines in the figure correspond to the concentrations of dissociating groups obtained from equation (4).

In order to raise the transport number and current efficiency of the synthesized membranes, it is necessary to increase the concentration of the dissociating groups in the membrane. However, without cross-linking, it is difficult to increase the concentration of dissociating groups because of the water content rise as shown in Table 1. On the other hand, if the water content is decreased by the cross-linking, it would be possible to increase the concentration of dissociating groups. However, cross-linking usually increases electric resistance. Therefore, we have to find the optimum conditions for increasing both the degree of grafting and the degree of cross-linking. The direction towards such optimum conditions is indicated by the arrow in Fig. 8. In addition, if we are able to make the structure of the membrane more rigid by the development of the cross-linking, the solute diffusion coefficient. the electro-osmosis coefficient and the concentration osmosis coefficient would be lowered.

CONCLUSIONS

The current efficiency of synthesized membranes was lower compared with that of commercial membranes. This is supposedly because the transport number of the synthesized membrane was low. In addition, the solute diffusion coefficient, the electro-osmosis coefficient and the concentration osmosis coefficient of the synthesized membranes were recognized to be higher with increasing degree of grafting.

In order to elevate the current efficiency of the synthesized membranes to the same level as commercial ones, the concentration of dissociating groups in the synthesized membrane should be increased. Such an improvement can be achieved by increasing both the ion-exchange capacity and the degree of cross-linking in the synthesized membrane. At the same time, it is important to avoid increasing the electric resistance of the synthesized membrane.

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