Modification of Transport Properties of Ion Exchange Membranes.XV. Preparation and Properties of Cation Exchange Membranes Having a Single Cationic Charged Layer on the Membrane Surface by Sulfonyl–Amide Bonding

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In order to prepare an excellent monovalent cation permselective cation exchange membrane, a polyethyleneimine (PEI) layer was formed with sulfonyl–amide bonding between PEI and sulfonyl chloride groups on one surface of the membrane. Two methods were tried: 1) one surface of the membrane reacted with PEI and the remaining sulfonyl chloride groups were hydrolyzed, and 2) after one surface of the sulfonyl chloride groups had been hydrolyzed, the other surface of the membrane was reacted with PEI and the remaining sulfonyl chloride groups were hydrolyzed. The cation exchange membranes, which had been prepared using both methods, had excellent monovalent cation permselectivity, low electrical membrane resistance and high current efficiency for the long-term electrodialytic concentration of seawater. The reacted amount of PEI on the membrane was about 10% of the cation exchange capacity.

Ion exchange membranes have been used for the electrodialytic concentration of seawater to produce edible salt. Especially, in the case of seawater concentration, monovalent ion permselective membranes versus the polyvalent and low electrical resistance of membrane are required to save energy and avoid the scaling problems of alkali earth metal compounds such as $CaSO_4 \cdot 2H_2O$.

In order to prepare the monovalent cation permselective membrane, various methods concerning the surface modification of the cation exchange membrane have been studied.[1)] One method was to adsorb or ion-exchange a cationic polyelectrolyte such as PEI, poly-*N*-methyl-4-vinylpyridinium chloride, on the surface of the cation exchange membrane.[2—9)] However, the monovalent cation permselectivity was gradually lost during long-term electrodialysis, since PEI was desorbed on the surface of the membrane. Therefore, it would be better if a stable chemical bond is formed between the cationic polyelectrolyte and the cation exchange membrane.

Thus, the fixation of a cationic polyelectrolyte on the surface of the cation exchange membrane was studied. For example, the sulfonyl–amide bonding between sulfonyl chloride groups of the membrane and PEI was formed of the surface of the membrane.[10—13)] These membranes exhibited a high monovalent cation permselectivity and also higher electrical resistance. In this case, sulfonyl chloride groups were introduced by the reaction of a mixture of chlorosulfuric acid and carbon tetrachloride with the precursor membrane, which was composed of a copolymer of styrene and divinylbenzene. Since the reaction of the membrane is severe when a high concentration of chlorosulfuric acid is used, the polymer matrix of the membrane might partially decompose. Therefore, we tried to introduce sulfonyl chloride groups into the precursor of the cation exchange membranes using moderate reaction conditions, that is, by use of a mixture of a lower concentration of chlorosulfuric acid in sulfuric acid.[14)] We also utilized precursor membranes composed of a copolymer of styrenesulfonyl chloride and divinylbenzene.[14)]

On the other hand, the membrane which reacted with PEI by sulfonyl–amide bonding showed a 5—8% lower current efficiency of the membrane than the membrane which was adsorbed on or ion-exchanged with PEI on the desalting side of the membrane during the electrodialytic concentration of the seawater. Furthermore, the electrical resistance of the membrane containing sulfonyl–amide bonding was high because the sulfonyl–amide layers existed on both sides of the membrane. Thus, in order to improve the current efficiency and the electrical resistance of the membrane, the preparation methods which form a single cationic polyelectrolyte layer on one surface of the membrane were studied. Also, the electrochemical properties, the reacted amount of PEI, the distribution of PEI and the electrodialytic concentration of the seawater of the resultant membranes were examined.

Experimental

1. Material. Membrane. The precursor membrane for the cation exchange membrane was prepared by the "paste method", that is, a mixture of styrene (90 parts), commercial divinylbenzene (10 parts), dioctylphthalate (30 parts), and benzoylperoxide (1 part) was copolymerized in the presence of polyvinyl chloride powder (50 parts) using polyvinyl chloride cloth as the support material.[15—19)] The precursor membrane and a monovalent anion permselective membrane (NEOSEPTA ACS) were provided by Tokuyama Corp. The membrane thickness was about 0.11—0.16 mm.

Reagents. Chlorosulfuric acid, sulfuric acid, sodium hydroxide, sodium chloride, calcium chloride, sodium molybdate dihydrate, and hydrochloric acid were of reagent grade: All were obtained from Wako Pure Chemical Industries Co., Ltd. Table 1 shows the characteristics of the PEI used in this work. PEI is believed to be highly branched, possessing primary, secondary, and tertiary amino groups in a ratio of approximately 1 : 2 : 1.[21)]

2. Reaction. **Introduction of Sulfonyl Chloride Groups.** The precursor membranes (7 cm×40 cm, 2 sheets) were immersed in a mixture (ca. 500 g) of 30—40% chlorosulfuric acid and 70—60% sulfuric acid at room temperature for 1 h. After the chlorosulfonylation, the membranes were successively washed with concentrated sulfuric acid, 80% sulfuric acid, 40% sulfuric acid, and pure water to avoid the generation of heat. The membranes were then stored in pure water at about 4 °C.

Surface Modification of the Membrane. In order to form a cationic polyelectrolyte layer on one surface of the membrane, one surface of the chlorosulfonylated membrane was reacted with an aqueous 10% PEI solution and then hydrolyzed with an aqueous 2.5 M (1 M = 1 mol dm^{-3}) NaOH solution. However, the one-surface reaction with PEI needed a long reaction time, while a short reaction time for the one-surface treatment was desirable for the manufacture of the membranes. Therefore, another one-surface reaction was studied. One surface of the chlorosulfonylated membranes was then reacted with an aqueous 2.5 M NaOH solution to convert the sulfonyl chloride groups into sodium sulfonic acid groups and then the other surface was reacted with the PEI.

This treatment was performed using the apparatus as shown in Fig. 1. Two sheets of the chlorosulfonylated membranes were set in the apparatus using a gum gasket and fastened with bolts. The apparatus was then soaked in an aqueous 10% PEI solution for 0.5—2 d or an aqueous 2.5 M NaOH solution for 10—60 min at room temperature. After the reaction, the apparatus was washed with pure water and the membranes were removed. Thereafter, these membranes were immersed in an aqueous 2.5 M NaOH solution to hydrolyze any remaining sulfonyl chloride groups for 2 h at room temperature. In the later case, after the hydrolysis, the membranes were immersed in an aqueous 10% PEI solution for 0.5—2 d and then soaked in an aqueous 2.5 M NaOH solution for 2 h at room temperature. The membrane having PEI layers on both surfaces were prepared by immersing the chlorosulfonylated membranes in an aqueous 10% PEI solution and then in an aqueous 2.5 M NaOH solution. After the hydrolysis, the membranes were washed with pure water, immersed in an aqueous 1 M HCl solution and then equilibrated with an aqueous 0.5 M NaCl solution before measurement.

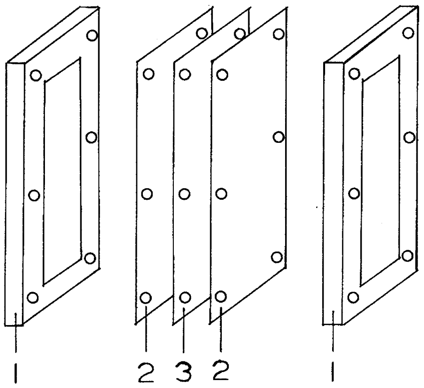

Fig. 1. An apparatus for one side treatment of membranes: (1) stainless frame, (2) precursor membrane, (3) gum gasket.

3. Measurements. The content of the sulfonyl chloride groups ($-SO_2Cl$) in the precursor membrane was measured as follows. After the chlorosulfonylation, there were two types of functional groups in the membrane, that is, sulfonyl chloride groups and sulfonic acid groups ($-SO_3H$). Hydrogen ions of the sulfonic acid groups ion-exchange with other cations such as sodium ions, whereas sulfonyl chloride groups are not ion exchange sites. Thus, the precursor membranes (5 cm×5 cm, 2 sheets) were washed several times with pure water at room temperature until the water showed no acidity. The membranes were then immersed in a 100 ml of an aqueous 3 M NaCl solution, and the concentration of H^+ ions exchanged by Na^+ ions was measured by acid-base titration. The remaining sulfonyl chloride groups in this membrane were then hydrolyzed into sulfonic acid groups with aqueous 2.5 M NaOH solution for 2 h at room temperature. The ion exchange capacity of the membranes, which were hydrolyzed into sulfonic acid groups, was determined as follows.[22)] The membranes were immersed in an aqueous 1 M HCl solution and then washed with pure water, and the concentration of H^+ ions was measured using the same method to determine the content of sulfonic acid groups in the precursor membrane. The membranes were equilibrated with an aqueous 0.5 M NaCl solution. An aqueous solution attached to the membrane was absorbed by filter paper; then the membranes were dried under vacuum and weighed. The content of sulfonyl chloride groups in the membrane is defined as:

$$[-SO_2Cl]/([-SO_2Cl]+[-SO_3H])$$
$$= 100 \times \frac{[\text{Ion exchange capacity}] - [-SO_3H]}{[\text{Ion exchange capacity}]} \ (\%).$$

where $[-SO_2Cl]$ means the sulfonyl chloride groups in the membrane (mequiv/g·dry membrane), $[-SO_3H]$ means the sulfonic acid groups in the membrane (mequiv/g·dry membrane), and the unit of ion exchange capacity is mequiv/g·dry membrane.

The electrochemical properties of the resulting cation exchange membranes, i.e., electrical resistance of the membrane and monovalent cation permselectivity, were measured. The electrical resistance of the membranes was measured with a 1000 cycle AC at 25 °C after the membrane had been equilibrated with 0.500 M sodium chloride solution.

The monovalent cation permselectivity against polyvalent ones was evaluated by the continuous electrodialytic concentration of

Table 1. Characteristics of PEI

Maker	Grade[a)]	η_{sp}/c (1.0%)[b)]	MW[c)]	MW[d)]
Sogo Pharmaceutical Co., Ltd.	Everamine 210T (50%)	0.125	1920	5000

a) PEI was supplied as an aqueous solution. Number in the parenthesis shows a concentration when it was supplied. b) Reduced viscosity was measured in a 1.0% aqueous solution at 25.0 °C. c) Calculated by equation $\eta_{sp}/c = 2.8\times10^{-4}\, M_w$ (c = mol dm^{-3}, 1.0% aqueous solution, 25.0 °C).[20)] d) Molecular weight shown officially by maker.

seawater. Electrodialysis was carried out using the poly-compartment electrodialyzer, which was a modified filter press type reported in a previous paper (the effective membrane area was 4 cm×25 cm).[23] The anion exchange membranes used were NEOSEPTA ACS made by Tokuyama Corp.; these have a permselectivity for chloride ions versus sulfate ions. The electrodialysis was carried out at the current density of 30 $\mathrm{mA\,cm^{-2}}$ at 30 °C and the linear flow velocity of seawater to the membrane surface was 6 $\mathrm{cm\,s^{-1}}$. The concentrated solution was periodically sampled after the composition of the concentrated solution had attained equilibrium. The seawater used in this study was obtained from Tokuyama Bay and the content of the main ions is shown in Table 2. The seawater was filtered using a sand filter in order to remove any suspended colloidal materials. The pH 8 seawater, and the pH 6.5 seawater which was controlled with hydrochloric acid, were used in this work.

Evaluation of the monovalent cation permselectivity was made by measuring the purity of the brine:

$$\text{purity of brine} = 100([\mathrm{Na^+}]+[\mathrm{K^+}])/[\mathrm{C^+}]\ (\%)$$

where $[\mathrm{Na^+}]$ and $[\mathrm{K^+}]$ are the concentration of sodium ions and potassium ions in the sampled concentrated solution respectively and $[\mathrm{C^+}]$ is the concentration of total cations in the concentrated solution. The sum of the concentration of sodium ions and that of potassium ions in the sampled solution was calculated by subtracting the concentrations of calcium ions and magnesium ions from those of the total cations. The concentrations of calcium ions and magnesium ions were analyzed using the conventional chelate titration method. Chloride ions were analyzed using Mohr's method and sulfate ions were analyzed by the gravimetric method using barium chloride.

Current efficiency during the electrodialysis of the seawater concentration was measured as follows:

$$\mathrm{C.E.} = 100([\mathrm{C^+}]VF/ISt)\ (\%)$$

$[\mathrm{C^+}]$ is the concentration of total cations in the concentrated solution (equivalent $\mathrm{cm^{-3}}$), V is the amount of overflow ($\mathrm{cm^3}$) from the concentrated solution chamber for a sampling period t (s), F is the Faraday constant, I is current density ($\mathrm{A\,cm^{-2}}$), and S is effective membrane area ($\mathrm{cm^2}$).

The IR spectra were recorded by the ATR (attenuated total reflection) technique using a Perkin–Elmer 1500 FTIR spectrometer in order to confirm the presence of sulfonyl–amide groups on the surface of the membrane. The distribution of PEI in the membrane was observed by attaching molybdate anions ($\mathrm{MoO_4^{2-}}$) to the amino groups of the PEI. The sample was prepared in the following manner. The membrane containing a single PEI layer was immersed in a slightly acidic aqueous 1% sodium molybdate solution for one day at room temperature. Thereafter, the membrane was washed with methanol and the specimen was prepared using an ultramicrotome. Finally, it was coated with a thin layer of carbon. The specimen was then observed using an electron probe micro-analyzer (JEOL JSM-50A). Both a scanning electron micrograph and a line scanning of the Mo $L\alpha$ X-ray profile were done over the same area on the membrane cross section.

Results and Discussion

Comparison of Membrane Properties between a Single and Double PEI Layer on the Membrane. The precursor membranes were reacted with 39.4% chlorosulfuric acid in sulfuric acid at room temperature for one hour. The content of the sulfonyl chloride groups ($\mathrm{-SO_2Cl}$) was 1.10 mequiv/(g·dry membrane), and the content of the sulfonic acid groups ($\mathrm{-SO_3H}$) was 1.05 mequiv/(g·dry membrane). One side of the chlorosulfonylated membranes was reacted with an aqueous 10% PEI solution for 0.5—2 d at room temperature using the apparatus shown in Fig. 1. These membranes were then immersed in an aqueous 2.5 M NaOH solution for 2 h at room temperature. Figure 2 shows the electrical resistance of the resultant membranes. The electrical resistance increased with increasing reaction time. Moreover, the two side treated membranes had a higher electrical resistance than the membranes with the single PEI layer. Since the sulfonyl–amide groups are not ion-exchangeable groups under this condition, the formation of the sulfonyl–amide bonding decreased the cation exchange capacity and increased the electrical resistance of the membrane. The cation exchange membrane, which did not react with the PEI, had about 2.15 mequiv/(g·dry membrane) of ion exchange capacity. When the membranes were reacted with the PEI, the cation exchange capacity of the membrane decreased with increasing reaction time, as shown in Fig. 3. For example, the cation exchange capacity decreased to about 1.9 mequiv/(g·dry membrane) using the one-surface reaction of the PEI. Also, the membranes containing PEI layers on both surfaces had smaller cation exchange capacities than these with only one surface treated.

The amount of PEI on the membrane was determined from an elemental analysis. Figure 3 shows the relationship between the amount of PEI (the amount of amino groups in PEI: mequiv/(g·dry membrane)) and the reaction time. It was found that the amount of PEI was almost equal to the

Table 2. Typical Composition of Seawater

Ionic species	Equivalent $\mathrm{dm^{-3}}$	$\{(\mathrm{A^-}$ or $\mathrm{C^+})$/total cation or anion$\}\times100$
$\mathrm{Cl^{-1}}$	0.523	90.28
$\mathrm{CO_3{}^{2-}}$ [a]	0.0023	0.40
$\mathrm{SO_4{}^{2-}}$	0.054	9.32
$\mathrm{Na^+}$	0.443	76.34
$\mathrm{K^+}$	0.0095	1.64
$\mathrm{Ca^{2+}}$	0.0198	3.41
$\mathrm{Mg^{2+}}$	0.108	18.61

a) Alkalinity of seawater (Seawater was titrated with 0.1 M hydrochloric acid until methylorange (indicator) changed to red color).

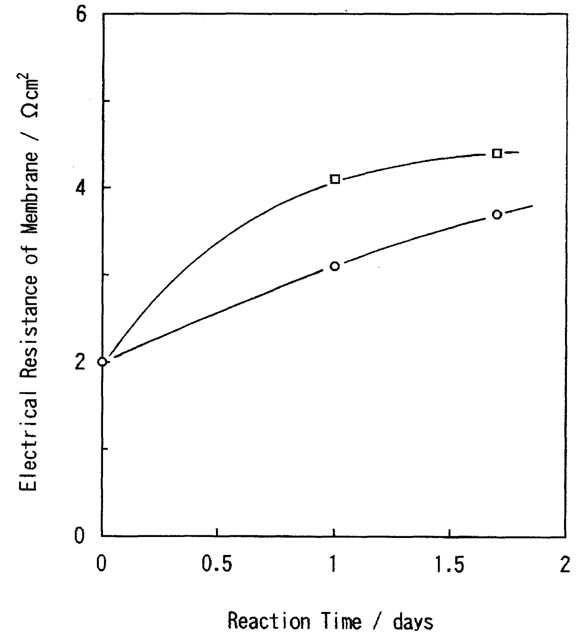

Fig. 2. Effect of one side or both side reaction time of an aqueous 10% PEI solution with chlorosulfonylated membranes on electrical resistance of membranes: ○ one side treatment, □ both side treatment. Chlorosulfonylation was carried out under $ClSO_3H/(ClSO_3H+H_2SO_4)$=39.4% for 1 h at room temperature.

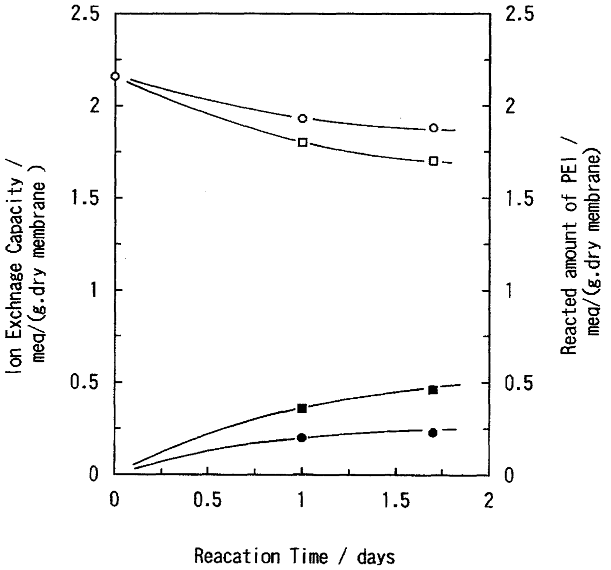

Fig. 3. Effect of one side or both side reaction time of an aqueous 10% PEI solution with chlorosulfonylated membranes on ion exchange capacity and reacted amount of PEI: ion exchange capacity, ○ one side treatment, □ both side treatment; reacted amount of PEI, ● one side treatment, ■ both side treatment.

decrease in the ion exchange capacity. Only one part of the primary and secondary amino groups of PEI reacted with the sulfonyl chloride groups to form sulfonyl–amide bonding, whereas the other part of the amino groups and tertiary amino groups of the PEI did not form sulfonyl–amide bonding and exited as free amino groups into the pores of the membrane. When the membrane containing the PEI was immersed in 1 M hydrochloric acid, there were sulfonic acid groups, sulfonyl–amide groups and the HCl salt of amino groups of the PEI in the membrane. After the membrane had been washed with pure water, the attached H^+ of the amino groups ($NH_3{}^+$, $NH_2{}^+$, NH^+) of PEI acted as counter cations toward the sulfonic anion groups ($-SO_3{}^-$) because of the disappearance of HCl. Then polysalts were formed among the sulfonic anion groups and attached H^+ of the amino groups in the PEI. Therefore, it was postulated that the amount of PEI on the membrane was equal to the amount of the sulfonyl–amide bonding and the polysalts.

Permselectivity. Figure 4 shows the permselectivity of the monovalent cations against the polyvalent ones and the current efficiency of the concentrated solutions when the resultant cation exchange membranes were used for the electrodialytic concentration of the seawater at pH 6.5. In the case of the membranes with a single PEI layer, the treated membrane surface faced the seawater side. The one-side and the two-side treated membranes produced a 95—97% purity brine. Therefore, it was found that the permselectivity of monovalent cations depended on the chemical structure of the surface of the membrane which faced the seawater side, that is, cations initially entered from the seawater to the membranes under the direct electrical field. When the one side of the membrane containing a thick PEI layer faced the concentrated solution chamber and the other side of the membrane containing only sulfonic acid groups faced the seawater chamber, the permselectivity of the monovalent cations was as low as about 80%.

Current Efficiency of Membrane. The current effi-

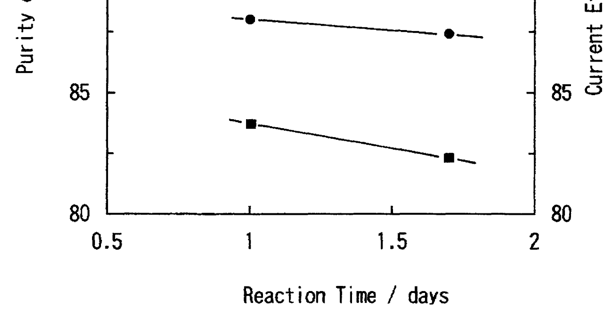

Fig. 4. Effect of one side or both side reaction time of an aqueous 10% PEI solution with chlorosulfonylated membranes on the purity of brine and current efficiency: purity of brine, ○ one side treatment, □ both side treatment; current efficiency, ● one side treatment, ■ both side treatment.

ciency during the electrodialytic concentration of seawater depends on the performance of the cation and anion exchange membranes. The current efficiency of the electrodialytic concentration of seawater is ordinarily about 90%. It was found that there were large differences in the current efficiency between the one-side treated membranes and two-side ones. Though the current efficiency of the one-side treated membranes was 87—88%, that of the two-side treated membranes was 82—83% as shown in Fig. 4. It was thought that these large differences were due to the sulfonic acid groups content on the concentrated solution side of the membrane which prevented the anions (Cl^-, SO_4^{2-}) from penetrating from the concentrated solution chamber through the membrane to the seawater chamber by the action of the Donnan exclusion of co-ions. When the thick cationic polyelectrolyte layer such as PEI existed on the concentrated solution chamber side of the membrane, the current efficiency decreased due to the decrease in the permselectivity of cations versus anions, that is, the lack of the Donnan exclusion for anions.

The Amount of PEI on the Membrane. Figure 5 shows the effect of the reacted amount of PEI on the permselectivity of $P_{\mathrm{Na}}^{\mathrm{Ca}}$. The membrane contained 0.06—0.08 mg cm^{-2} of PEI for a single PEI layer membrane and 0.12—0.15 mg cm^{-2} of PEI for the double PEI layered membrane. On the contrary, it was reported that the amount of adsorbed or exchanged PEI (21OT) on the cation exchange membrane (NEOSEPTA CL-25T) from an aqueous 0.1% PEI solution for 24 h at 25 °C was about 0.032 mg cm^{-2}.[2)] It was found that the thick PEI layer was formed on the surface of the membrane by the reaction between the sulfonyl chloride groups on the membrane and an aqueous 10% PEI solution. The PEI layer formed by the adsorption or exchange method on the cation exchange membrane was a thinner layer than that which formed when using the reaction method.

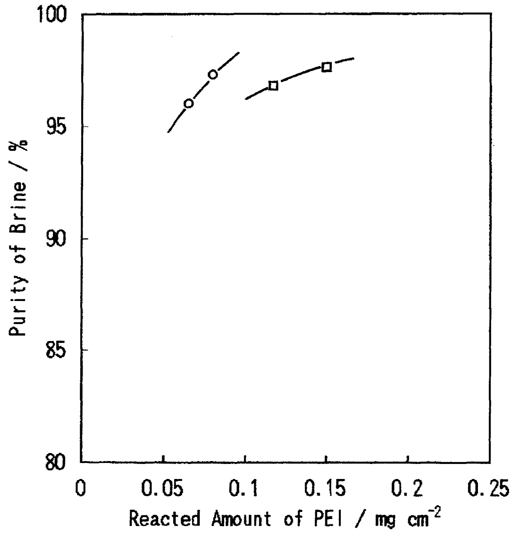

Fig. 5. Relationship between reacted amount of PEI and purity of brine: ○ one side treatment, □ both side treatment.

ATR Spectrum of the Membranes. The ATR spectra of the chlorosulfonylated membrane, sulfonic acid-formed

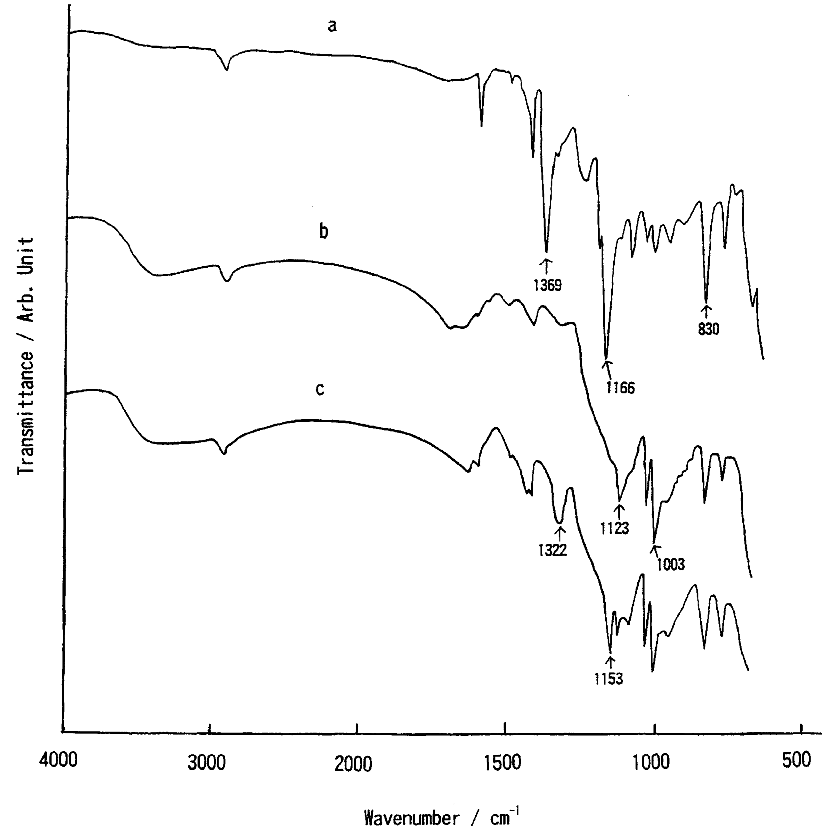

Fig. 6. ATR spectrum of chlorosulfonylated membrane (a), sulfonic acid form membrane (b), and membrane modified with PEI (c).

membrane and the membrane modified with PEI after drying the membrane in a vacuum are shown in Fig. 6. The absorption band assigned to the sulfonyl chloride groups were observed as a S=O stretching vibrations at 1369 and 1166 $\mathrm{cm^{-1}}$. Also, the sulfonic acid groups were at 1123 and 1003 $\mathrm{cm^{-1}}$. After the reaction of the PEI, the absorption band of the sulfonyl chloride groups completely disappeared, and the new absorption band of the sulfonyl–amide groups were observed as a S=O stretching vibrations at 1322 and 1153 $\mathrm{cm^{-1}}$. The absorption band of 830 $\mathrm{cm^{-1}}$ was due to 1,4-substituted aromatic groups. Though the formation of sulfonyl–amide groups was evident, the contents of sulfonyl–amide groups have been investigated.

Hydrolysis of Sulfonyl Chloride Groups on One Surface and Reaction of PEI with the Other Surface. Figure 7 shows the relationship between the value of $-\mathrm{SO_2Cl}/(-\mathrm{SO_2Cl}+-\mathrm{SO_3H})$ before hydrolysis of the chlorosulfonylated membranes and after their hydrolysis in an aqueous 2.5 M NaOH solution for 15 min at room temperature. The content of $-\mathrm{SO_2Cl}/(-\mathrm{SO_2Cl}+-\mathrm{SO_3H})$ in the membranes after the hydrolysis were almost half as much as the original chlorosulfonylated membranes. Also, it was confirmed that sulfonyl chloride groups remained on the unreacted side of the membranes by ATR.

After the hydrolysis of the one surface, the membranes were immersed in an aqueous 10% PEI solution for 16 h at room temperature to form a cationic polyelectrolyte layer on the other surface of the membranes. In order to obtain an excellent permselective ion exchange membrane, the relationship between the hydrolysis reaction time and the performance of the membranes were examined. The purity of the monovalent cations in brine was almost a constant value of 97—98% for 0—60 min of the hydrolysis reaction in pH 6.5 seawater, as shown in Fig. 8. The membrane, which had both sides of the membrane treated with PEI showed an 82% value of current efficiency. However, the current efficiency of the one-side treated membranes, which were hydrolyzed by the NaOH solution for 5 —60 min, had a normal value of 89—90%. The electrical resistances of the one-side treated membranes were almost a constant value 3—3.5 $\Omega\,\mathrm{cm^2}$.

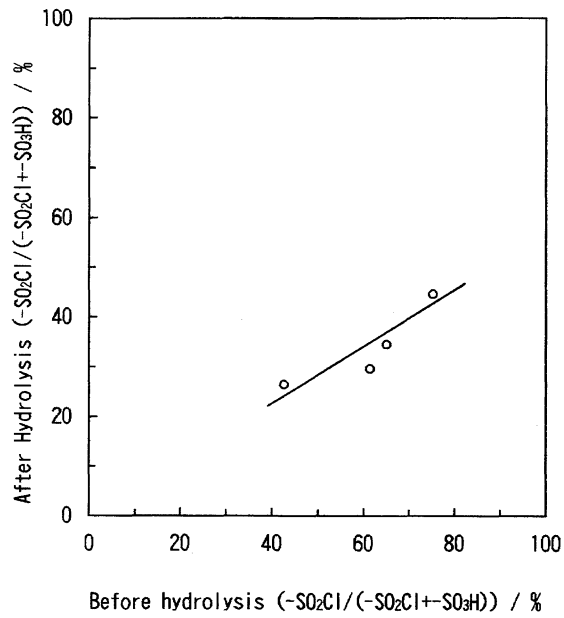

Fig. 7. Relationship between $-\mathrm{SO_2Cl}/(-\mathrm{SO_2Cl}+-\mathrm{SO_3H})$ before hydrolysis of chlorosulfonylated membranes and after their hydrolysis in an aqueous 2.5 M NaOH solution for 15 min at room temperature.

Distribution of PEI in the Membrane. Figure 9a shows the scanning electron micrograph of the cross section of the membrane with a single PEI layer. The modified membrane was prepared from the hydrolysis of an aqueous 2.5 M NaOH solution for 15 min and then reacted with the PEI for 16 h. Figure 9b shows the distribution of the attached molybdate anions on the amino groups of the PEI in the cross section part of the membrane designated by the arrow in Fig. 9a. It was found that there was a single molybdenum peak on the one side of the membrane. The molybdenum peak was high at the surface, gradually decreased and disappeared at the inner part of the membrane. The molybdenum peak width, that is, (PEI layer)/(membrane thickness), was about 0.18. The molybdenum peak was not found on the hydrolyzed side of membrane, because the sulfonyl chloride groups were completely hydrolyzed and the absorbed or ion-exchanged PEI were easily eliminated from the surface of the membrane by the severe hydrolysis conditions. These results showed that the short 15-min hydrolysis reaction on the one surface of the membrane was enough to fix PEI on the other surface of the membrane and to prepare an excellent permselective cation exchange membrane.

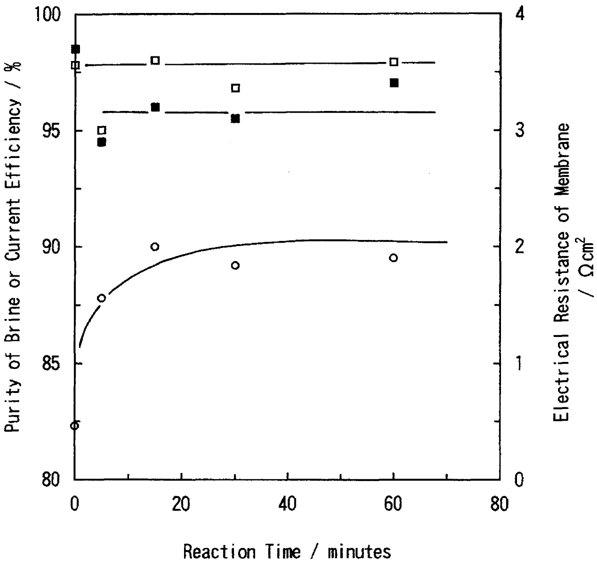

Fig. 8. Relationship between one side hydrolysis reaction time by an aqueous 2.5 M NaOH solution and properties of membrane: □ purity of brine, ○ current efficiency, ■ electrical resistance of membranes. Chlorosulfonylation reaction conditions were $\mathrm{ClSO_3H}/(\mathrm{ClSO_3H}+\mathrm{H_2SO_4})=36.7\%$ for 1 h at room temperature. Precursor membranes were reacted with an aqueous 10% PEI solution for 16 h at room temperature.

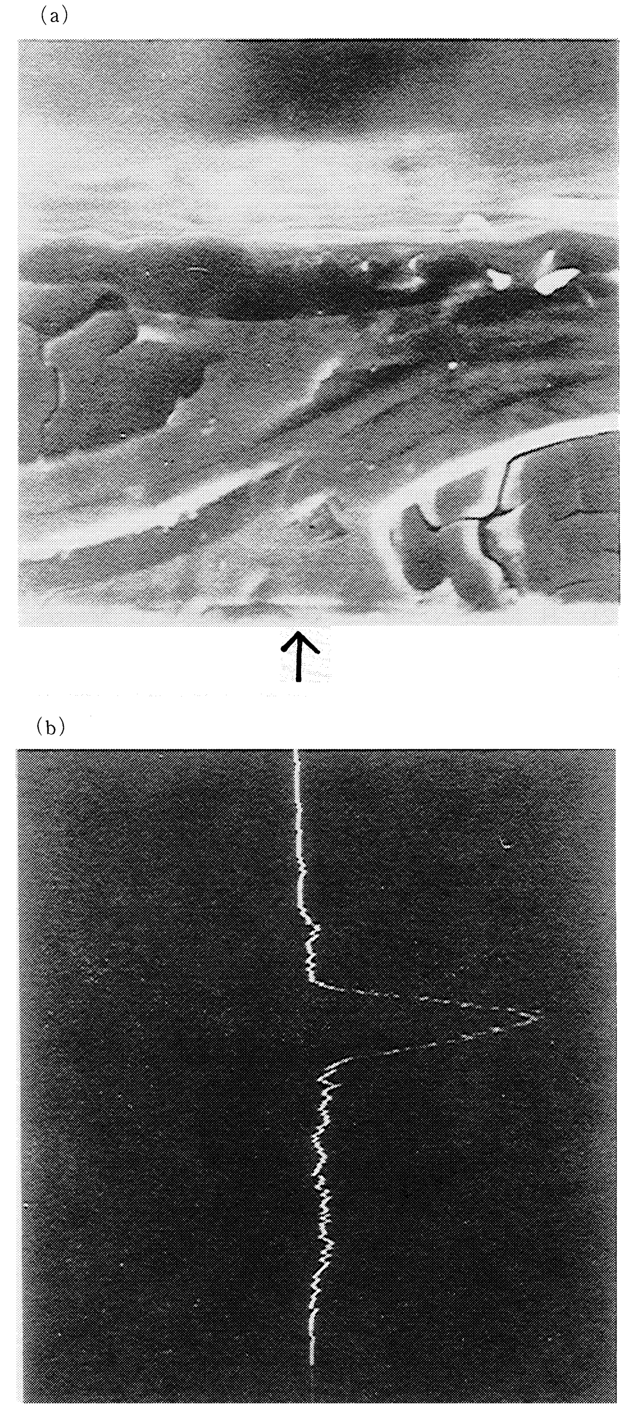

Fig. 9. (a) Scanning electron micrograph of the crossection of the membrane with a single PEI layer. (b) Distribution of attached molybdate anions in the membrane with a single PEI layer.

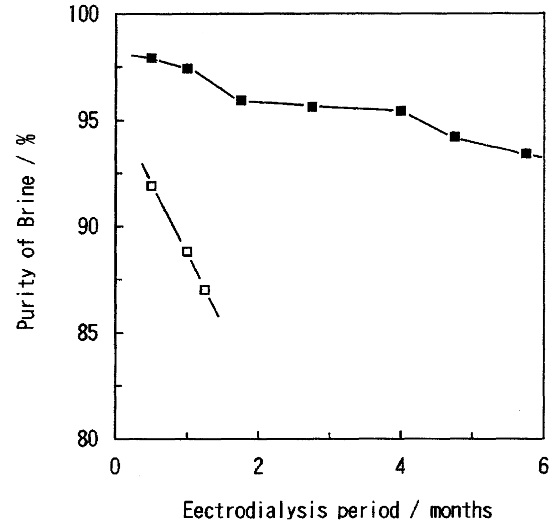

Fig. 10. Durability of purity of brine: □ seawater pH 8, ■ seawater pH 6.5. Chlorosulfonylation reaction conditions were $ClSO_3H/(ClSO_3H+H_2SO_4)=36.7\%$ for 1 h at room temperature. One side hydrolysis was carried out under an aqueous 2.5 M NaOH solution for 15 min at room temperature. PEI treatment was carried out an aqueous 10% PEI solution for 16 h at room temperature.

Durability of Permselectivity of the Membrane during the Electrodialysis of Seawater. Figure 10 shows the maintenance of brine purity of the resultant membranes during the electrodialysis concentration of seawater (the seawater pH: 8 or 6.5), which were modified by PEI after the membranes had been hydrolyzed by an aqueous 2.5 M NaOH solution for 15 min. The purity of brine gradually decreased in the slightly basic seawater (pH: 8). Because PEI contains weakly basic amino groups, these weakly basic groups on the surface of the membranes lost attached H^+ to the amino groups in long contact with the slightly basic seawater. Therefore, the PEI layer gradually weakened the electrical repulsion force against polyvalent cations compared to the monovalent cations and thus allowed the polyvalent cations to gradually permeate through the membrane.

In the slightly acidic seawater (pH 6.5), the purity of brine of monovalent cations slightly decreased after several months. The purity of brine was maintained at above 90% for 6 months. Also, the current efficiency of the concentrated salt solution was almost a constant value of 88—91% for 6 months during continued seawater concentration. It was thought that the decrease in the permselectivity depended on the release of attached hydrogen ions to the weak amino groups in PEI, the desorption of absorbed PEI, or the decomposition of PEI on the membrane.

It was ascertained that the one-side treatment was a useful method to prepare excellent monovalent cation permselective cation exchange membranes for long-term electric concentration of the slightly acidic seawater.

Conclusions

1. The formation of the sulfonyl–amide bond with the reaction with PEI resulted in an decrease in the cation exchange capacity and an increase in the electrical resistance of the membranes. The reacted amount of PEI was equal to the decrease in the cation exchange capacity.

2. There are two methods to fix the PEI layer on one side of the membrane. One method was that one side of the chlorosulfonylated membranes reacted with PEI. The second was that one side of the chlorosulfonylated membrane was

hydrolyzed with an aqueous NaOH solution and then reacted with PEI. The PEI layer in the membrane was confirmed by the observation of the line scanning of the Mo $L\alpha$ X-ray profile of the attached MoO_4^{2-} to PEI.

3. The one-surface and the two-surface reacted membranes with PEI showed excellent permselectivity of the monovalent cations. But, the two-surface reacted membrane with PEI showed a 5—8% lower efficiency than the one-surface treated membranes.

4. The one-sided modified membranes with PEI exhibited a high permselectivity of monovalent cations and a normal current efficiency for about 6 months in the slightly acidic seawater.

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