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Preparation and Transport Properties of Composite Membranes Composed of Cation Exchange Membranes and Polypyrrole

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ABSTRACT: Composite membranes composed of cation exchange membranes and polypyrrole, in which polypyrrole existed on one surface of the membrane as a thin layer, were prepared with ferric ion form cation exchange membranes and an aqueous pyrrole solution. After confirming the existence of the polypyrrole layer on the membrane surface (EPMA, conductivity, and micrograph), the following electrodialytic transport properties of the membrane were evaluated: the electrical resistance of the membrane, the relative transport number between the alkali earth metal cations and sodium ions, the current efficiency, and voltage drop at the membrane. The permeation of calcium ions was markedly decreased by the formation of a polypyrrole layer on the cation exchange membranes in both cases where the layer faced the anode and the cathode compartments. It was confirmed by a decrease in the current efficiency during electrodialysis in the layer facing the cathode compartment that the polypyrrole layer has a cationic charge. The permeability coefficient of the neutral molecules through the membrane was markedly decreased by the formation of a layer on the cation exchange membrane. From these results, a decrease in the permeation of the alkali earth metal cations versus sodium ions was observed based on the synergistic effect of the sieving of divalent cations by a tight and rigid polypyrrole layer and the difference in the electrostatic repulsion force between the divalent cations and the sodium ions.

Introduction

An ion exchange membrane is one of the most advanced separation membranes and has been used in various industrial fields. Though the electrochemical properties of the membrane such as transport number, electrical resistance, diffusion coefficient of electrolytes, etc., have been vastly improved and have attained almost limiting values, several unsolved problems remain such as the lack of anti-organic fouling,[1] the abnormal permeation of acids through the anion exchange membrane by a concentration gradient,[2] the instability of anion exchange groups, quaternary ammonium groups, in a concentrated alkali solution,[3] the lack of the selective permeation of a particular ion,[4] etc.

On the other hand, conducting polymers such as polyaniline, polypyrrole, polythiophene, etc., are also one of the interesting functional polymers which have been studied[5−9] and used in some industrial fields.[10] These polymers are prepared by polymerizing their corresponding monomers such as aniline, pyrrole, thiophene, etc., using electrochemical[5] or chemical oxidation.[7] When both functional polymers, the ion exchange membrane and the conducting polymer, are combined, it is possible to manufacture various new functional membranes and materials. Especially, among these, pyrrole has a good affinity for ion exchange membranes and is easily and rapidly polymerized using chemical oxidation. It has been reported that a composite membrane composed of an anion exchange membrane and polypyrrole yields an anion exchange membrane with a high acid retention in an electrodialytic concentration of hydrochloric acid[11] and an anti-organic fouling property suitable for electrodialysis.[12] Also, the composite membranes prepared from anion or cation exchange membranes with polypyrrole layer are effective during the dehydration of a mixed water−alcohol solution using the pervaporation method.[13] The composite membrane has also been investigated as a gate membrane.[14] The composite membranes of the ion exchange membranes and the conducting polymers not only show such interesting properties as a separation membrane, but also provide new functional materials for other applications, such as a potentiometric humidity sensor,[15] etc.

To give the ion exchange membranes the ability to permeate specific ions, various methods have been tried, and some of these have been used in industry.[4] A composite membrane composed of a cation exchange membrane and polypyrrole is interesting from the viewpoint of the selective permeation of specific cations, because polypyrrole is a highly rigid and tight polymer with weakly basic anion exchange groups. It has been reported that when a ferric ion form cation exchange membrane is immersed in an aqueous pyrrole solution, the pyrrole is oxidized by the ferric ions ion-exchanged with the membrane, and a polypyrrole layer is formed on the membrane surface according to the polymerization conditions.[16] This is based on the fact that a polypyrrole layer formed on the membrane surface is too tight and therefore restricts the permeation of pyrrole molecules into the interior of the membrane. It is interesting to note the change in the transport properties for the cation exchange membranes with a thin polypyrrole layer.

In this work, after the cation exchange membranes, which are commercially available, had been converted in the ferric ion form, one surface of the membrane was placed in contact with an aqueous pyrrole solution to form a thin polypyrrole layer on the surface. The electrodialytic transport properties of the resultant composite membranes were then evaluated in detail.

Experimental Section

Materials. a. Cation Exchange Membranes. Commercial cation exchange membranes, NEOSEPTA CM-1, produced by Tokuyama Corp., and Nafion 117, produced by E. I. du Pont de Nemours & Co. (Inc.), were used to anisotropically prepare the cation exchange membranes having a polypyrrole layer (composite membrane). The characteristics

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Table 1. Characteristics of Cation Exchange Membranes Used in this Study

membrane	NEOSEPTA CM-1	Nafion 117
thickness (mm)	0.145	0.175
electric resist.[a]	1.43	3.50
ion exchange capacity[b]	2.24	0.92
water content[c]	35.8	22.0
fixed ion concn[d]	6.26	4.18
transport number[e]	98	95

[a] Ω·cm^2; measured with 1000 Hz AC at 25.0 °C after equilibrating with a 0.500 N sodium chloride solution. [b] mequiv/g of dry membrane in Na^+ form. [c] g of H_2O/g of Na^+ form dry membrane. [d] (Ion exchange capacity/water content) × 100. [e] Measured by electrodialysis with a 0.50 N sodium chloride solution at 2 A/dm^2 at 25.0 °C.

of the cation exchange membranes used in this work are shown in Table 1. Before use, the NEOSEPTA CM-1 was equilibrated in a 0.5 N sodium chloride solution and a 1.0 N hydrochloric acid solution alternatively several times. The acid form membrane was equilibrated with a 0.50 N ferric chloride solution (the ferric chloride solution was renewed until the pH of the solution attained the intrinsic value of the solution). The Nafion membrane was prepared by heating in boiling water for more than 30 min. The membrane was then equilibrated in a 0.5 N sodium chloride solution alternated several times with a 1.0 N hydrochloric acid solution. The membrane was then equilibrated with a 1.11 N ferric chloride solution.

b. Chemicals. Reagent grade sodium chloride, calcium chloride, magnesium chloride, strontium chloride, barium chloride, hydrochloric acid (35%), ammonia solution (29%), pyrrole, $FeCl_3 \cdot 6H_2O$, hydrobromic acid, methyl alcohol, urea, glucose, saccharose, etc., which were obtained from the Wako Pure Chemical Industries Co., Ltd., were used without further purification. The concentration of each salt solution was determined using the Mohr method or by conventional chelate titration.

Preparation of Cation Exchange Membranes with a Polypyrrole Layer. A two compartment cell was used to anisotropically form a polypyrrole layer on one surface of the cation exchange membrane. After the ferric ion-form cation exchange membrane had been placed in the two compartment cell (the effective membrane dimensions were 8.0 cm × 15.0 cm), one surface of the membrane was sealed with a polyester film and the other side was placed in contact with an aqueous 0.745 mol/L pyrrole solution (240 cm^3), which was vigorously stirred for a given period. The ferric ions ion-exchanged with the sulfonic acid groups of the membrane acted as an oxidative agent to polymerize pyrrole at the membrane surface, and a polypyrrole layer was formed on the surface. It was confirmed that the ferric ions in the membrane were reduced to ferrous ions after the formation of the polypyrrole layer. After the polymerization of pyrrole on the membrane surface, the membrane was removed from the cell and washed with pure water followed with a thorough rinse of a 1.0 N hydrochloric acid solution to remove the ferric and ferrous ions. The obtained membrane was stored in a 1.0 N hydrochloric acid solution and equilibrated before use with the solution to be used in the measurement.

Because polypyrrole is a conducting polymer, the conductivity of the composite membrane was measured using the membranes manufactured with different polymerization times. After the ferric ion form membrane (5.0 cm × 5.0 cm) had been immersed in a 0.745 mol/L pyrrole solution for various periods (polypyrrole layers were formed on both surfaces), the membrane was completely washed with pure water followed by methyl alcohol and then completely dried under vacuum.

Measurements. a. Apparatus. A two compartment cell with silver−silver chloride electrodes, as shown in Figure 1, was used to measure the electrodialytic transport properties of the composite membranes. Two kinds of electrodes were contained in the cell: one for current supply (dimensions were 4.0 cm × 10.0 cm and it was bent in a wave-like shape) and the other for the measurement of the voltage drop at the membrane (silver−silver chloride wire probe electrodes which were placed 2 mm apart from the membrane surface). The effective membrane area was 10 cm^2 (2.0 cm × 5.0 cm), and the capacity (volume) of each compartment was 100 cm^3. Both compartments were vigorously stirred with stirrers (1500 ± 100 rpm) during the electrodialysis.

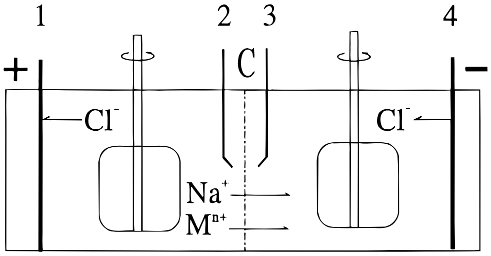


Figure 1. The apparatus for electrodialysis used in this work. C: composite membrane; 1 and 4: Ag−AgCl electrodes; 2 and 3: Ag−AgCl probe electrodes; effective membrane area: 10 cm^2.

The electricity that passed through the membrane was measured using a Nikko Digital Coulometer NDCM-4, Nikko Keisoku Ltd. The voltage drop at the membrane was measured with the silver−silver chloride probe electrodes and recorded on an EPR-2T X-t recorder from Toa Electronics Co.

b. Measurement of the Properties of the Composite Membranes. The electrical resistance of the composite membrane was measured using a 0.500 N sodium chloride solution and a 0.500 N calcium chloride solution. The measurement was made using 1000 cycle AC, Hewlett Packard LCR meter, LCR-4263A, at 25.0 °C.

The transport properties of the cation exchange membrane with the polypyrrole layer measured in this work were relative transport number between the two cations, current efficiency, and voltage drop at the membrane. The relative transport number was defined as follows:

$$P_{\mathrm{Na}}{}^{\mathrm{M}} = \frac{t_{\mathrm{M}}/t_{\mathrm{Na}}}{C_{\mathrm{M}}/C_{\mathrm{Na}}}$$

where t_{M} and t_{Na} are the transport numbers of the cation, M, and the sodium ions in the membrane, respectively, and C_{M} and C_{Na} are the average concentrations of the cation, M, and sodium ions before and after electrodialysis, respectively. $P_{\mathrm{Na}}{}^{\mathrm{M}}$ is the permeated equivalent of the cation, M, through the membrane when 1 equiv of sodium ions permeates the membrane (based on a 1:1 solution used for all experiments).

c. Electrodialysis Procedure. After the cation exchange membrane had been placed in the cell, both compartments of the cell were filled with 100 cm^3 of a mixed salt solution (at a 1:1 ratio). The cases used were magnesium chloride with sodium chloride, calcium chloride with sodium chloride, strontium chloride with sodium chloride, and barium chloride with sodium chloride. Though the concentration of the solution was mainly 0.5 N as chloride ion concentration, this concentration was changed for calcium chloride with sodium chloride (0.05, 0.10, and 0.50 N). The electrodialysis was carried out at a current density of 10 mA/cm^2 (for the 0.5 N solution) for 60 min at 25.0 °C. When the concentration of the solution was changed, the current density was adjusted according to the concentration (0.05 N: 2 mA; 0.1 N: 5 mA). In electrodialysis, the polypyrrole layer of the membrane normally faced the desalting side (anode compartment); however, the current was also passed from the opposite direction to examine effect of the layer on the transport properties.

After electrodialysis, the solutions were analyzed using the Mohr method for Cl^- and conventional chelate titration for alkali earth metal cations. The concentration of the sodium ions was calculated by subtracting the concentration of alkali earth metal cations from that of chloride ions. Thus, the relative transport number was calculated from the change in concentration of the cations in each compartment, and the current efficiency was calculated from the change in the concentration of the total cations. The electricity to pass the membrane was measured using a coulometer.

d. Measurement of Permeability Coefficient of Neutral Molecules. To estimate the change in the pore size for the membranes caused by the formation of the polypyrrole layer, the permeability coefficient of the neutral molecules, urea, glucose, and saccharose, was measured. The measurement was carried out in a two compartment cell that was vigorously agitated (1500 ± 100 rpm) at 25.0 °C. After an aqueous solution of each neutral molecule (urea, 2 mol/L; glucose, 2 mol/L; saccharose, 1 mol/L) had filled the concentrated compartment of the cell (250 cm^3) and pure water had filled the diluted compartment (100 cm^3), the amount of the neutral molecule that permeated into the water was analyzed (diffusion time, urea, 48 h; glucose, 72 h; saccharose, 96 h). Each neutral molecule was analyzed using an HPLC (Hitachi L-6000, RI Monitor L-3350), and the permeability coefficient was calculated using the following equation:

$$P = \frac{\Delta m}{At(C_C - C_D)}$$

where Δm is the permeated amount of the neutral molecule (equiv), A, the effective membrane area (20 cm^2), t, the diffusion time (s), C_C, the average concentration in the concentrated compartment during the dialysis, and C_D, the average concentration in the diluted compartment.

e. Analysis of the Cation Exchange Membranes with a Polypyrrole Layer. The existence of a layer of polypyrrole on the surface of the cation exchange membrane was confirmed by measuring the distribution of bromide ions using an EPMA (electron probe micro analysis), a JEOL JXA-8621M instrument. After the membrane had been equilibrated with a 1.0 N hydrobromic acid solution to dope and ion-exchange bromide ions to the pyrrole unit of the layer, the membrane was washed with methyl alcohol and completely dried. Carbon was then deposited on the membrane surface (200 Å) using vacuum evaporation to make the membrane surface conductive (JEOL JEE-450D apparatus). The membrane was fixed in epoxy resin (Araldite, Ciba-Geigy) and ground with a MA-200 grinding apparatus from Musashino Electronics Co., Ltd., to obtain a cross-section. The cross-section of the membrane was also observed using a microscope to confirm its anisotropicity. The difference is easily noted because the polypyrrole is black and the cation exchange membrane is transparent.

The conductivity of the composite membranes (where the polypyrrole layers existed on both surfaces) was measured to examine the degree of polymerization of the pyrrole on the membrane surface. A strip of the composite membrane (5.0 cm × 1.0 cm × 0.0135 cm) was used to measure the conductivity parallel to the plane of the membrane. These strips were cut from several places (original size was 5.0 cm × 5.0 cm). A coating of silver conductive paste (Electroconductive DOTITE D-550 made by Fujikura Kasei Co., Ltd.) was placed on both sides of the ends of the strips (10 mm length each), and a 1.0 cm × 1.0 cm window at the center of each strip was not coated. To measure the conductivity, the coated ends of the strip were tightly clamped between two platinum plates. Voltage was applied to both ends at the platinum plates using a potentiostat/galvanostat HA-303 from Hokuto Denko, Ltd., and the current which passed through the strip was measured with an HM-105 zero shunt ammeter from Hokuto Denko, Ltd. The voltage was increased from 1.0 to 4.0 V and measured with an HE-104 electrometer from Hokuto Denko, Ltd., and the current was recorded. The conductivity was calculated from the slope of the voltage−current relationship. The measurements were carried out in a desiccator of less than 20% relative humidity at 25 ± 1 °C.

The ferric and ferrous ions in the composite membrane (the layers existed on both sides), which had been stored in nitrogen atmosphere, were determined after eluting the iron ions from the membrane with a 0.5 N sodium chloride solution (the membrane was immersed in the 0.5 N sodium chloride solution under stirring, and the solution was renewed several times). The eluent was divided into two parts, and an aqueous solution of 1,10-phenanthroline (0.5% solution adjusted to pH 2) was added to one of the solutions. Ascorbic acid was added to the other part to reduce the ferric ions to the ferrous, and then 1,10-phenanthroline was added to that solution too. The concentration of a ferrous−1,10-phenanthroline complex (maximum absorption: 510 nm)[17] was determined by a UV−vis double-beam spectrophotometer UV-1600, Shimadzu Corp.

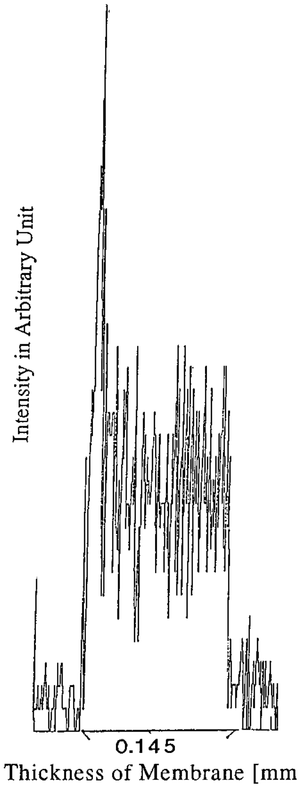


Figure 2. The EPMA of a cross-section of the composite membrane manufactured from NEOSEPTA CM-1 and pyrrole (polymerization time: 60 min). The membrane was equilibrated with an aqueous 1.0 N hydrobromic acid solution and washed with methyl alcohol.

Results and Discussion

1. Formation of a Polypyrrole Layer on a Surface of Cation Exchange Membranes. When one surface of a ferric ion form cation exchange membrane was exposed to an aqueous pyrrole solution, the pyrrole polymerized, and depending on the amount of ferric ions ion-exchanged with sulfonic acid groups of the membrane, the polypyrrole should exist on the membrane surface. (The ratio of the ferric ions to the hydrogen ions in the membrane was dependent on the concentration of the ferric chloride solution because the pH of the solution changed with the concentration.) To confirm the formation of the polypyrrole layer, the EPMA for a cross-section of the membrane was measured using membranes for which the polymerization time was 10 min, 1.0 h, and 12 h. (The concentration of the equilibrated ferric chloride solution was 0.5 N.) Figure 2 shows the EPMA result for the membrane which was in contact with the pyrrole solution for 1.0 h. The intensity of the bromide ions for a cross-section of the membrane was not so remarkably different in relation to polymerization time. Since pyrrole is a weakly basic compound, the molecule ought to ion-exchange rapidly with the sulfonic acid groups in the membrane and polymerize in the inner part of the membrane even if the ion-exchange reaction occurs from only one surface of the membrane. However, the thickness of the poly-

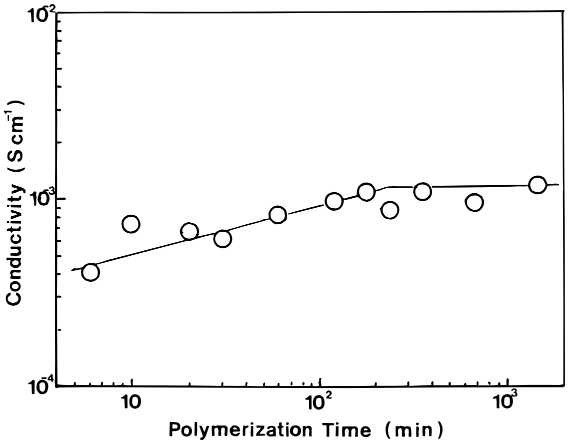


Figure 3. The change in the conductivity of the composite membranes versus polymerization time. The ferric ion form cation exchange membrane, NEOSEPTA CM-1, was immersed in an aqueous 0.745 N pyrrole solution.

pyrrole layer did not increase rapidly with an increase in the polymerization time. It was reported that when a ferric ion form cation exchange membrane is exposed to the aqueous pyrrole solution, polypyrrole slowly grows from the membrane surface toward the inner part of membrane.[16] This is based on the fact that the penetration of the pyrrole molecule into the membrane is retarded because the polypyrrole layer initially formed is too rigid and tight.

It was confirmed from the measurement of electrical conductivity that when the cation exchange membrane, NEOSEPTA CH-45T, which has a relatively high water content, i.e., more porous, in comparison with the NEOSEPTA CM-1, was immersed in an aqueous pyrrole solution, the polypyrrole layers which grew from both surfaces were connected at the middle of the cross-section of the membrane after 4 h of immersion.[18] A similar measurement was made using the NEOSEPTA CM-1. Though the cation exchange membrane of the ferric ion form is an insulator, only 1 min immersion in an aqueous pyrrole solution changed the membrane surfaces into an electrical conductor. Since it was impossible to separate the polypyrrole from the membrane matrix, the electrical conductivity of the composite membrane was measured to characterize the polymer. Figure 3 shows the change in conductivity for the composite membrane versus polymerization time (immersion period in the pyrrole solution). The conductivity of the membrane increased up to about 4 h and then attained an almost constant value. This is a phenomenonon similar to that reported in a previous paper[18] (in a composite membrane of short polymerization time, electricity passed only through the membrane surfaces). The polymer showed an almost similar conductivity to those previously reported.[18]

Since pyrrole was oxidized by ferric ions, the ferric ions in the membrane changed in ferrous ions after the formation of the layer. From the analysis of the ferric and ferrous ions in the membrane, the equivalent ratio of iron ions to the ion-exchange capacity of the membrane was unity. This means that the iron ions were released from the membrane during the polymerization process and balanced the charge of the membrane. Namely, the polypyrrole in the membrane was primarily doped with the chloride ions and the ferric chloride ions, not the sulfonic acid groups from the membrane.

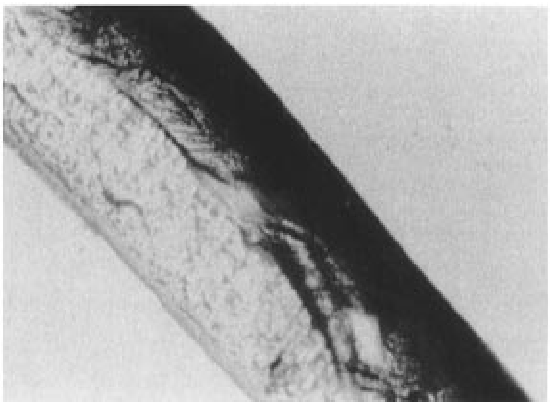


Figure 4. A microscopic photograph of a cross-section of a composite membrane (NEOSEPTA CM-1 and polypyrrole; polymerization time: 4 h).

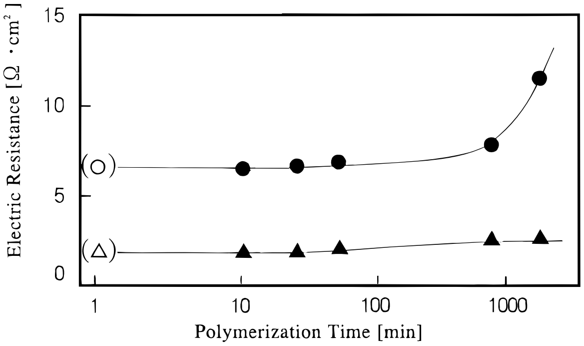


Figure 5. The change in the electrical resistance of the composite membrane (NEOSEPTA CM-1 and polypyrrole) versus polymerization time. ▲: measured in a 0.500 N NaCl solution; ●: measured in a 0.500 N $CaCl_2$ solution; △: NEOSEPTA CM-1 in a 0.500 N NaCl solution; ○: NEOSEPTA CM-1 in 0.500 N $CaCl_2$ solution. The membranes were equilibrated with a 1.0 N HCl before equilibration in a mixed salt solution.

It is thought that since the polymerization speed of the pyrrole is slow within the matrix of the cation exchange membrane based on the conductivity results, a thin polypyrrole layer is easily formed on the membrane surface by means of chemical oxidation polymerization. Figure 4 also shows a microscopic photograph of a cross-section of the membrane after 4 h of polymerization. Though the polypyrrole (black part) grew into the inner part of the membrane, a cation exchange membrane with a polypyrrole layer was obtained even after 4 h of polymerization. The obtained composite membrane is a kind of bipolar ion-exchange membrane because polypyrrole contains secondary amino groups. The layer should be thin to avoid a pH change in the solution due to acceleration of water dissociation at the interface between the layer and the cation exchange membrane during electrodialysis when the layer is facing to the desalting side (anode compartment).

2. Change in Electrochemical Properties of Cation Exchange Membranes with a Polypyrrole Layer. Figure 5 shows the change in the electrical resistance of the cation exchange membrane with a polypyrrole layer versus polymerization time. The electrical resistance was measured in a 0.500 N sodium chloride solution and a 0.500 N calcium chloride solution after immersing the membranes into a 1.0 N hydrochloric acid solution (the secondary amino groups of the polypyrrole were partially dissociated). The resistance measured in the sodium chloride solution increased very slightly with an increase in polymerization time. However, the resistance measured in the calcium chloride

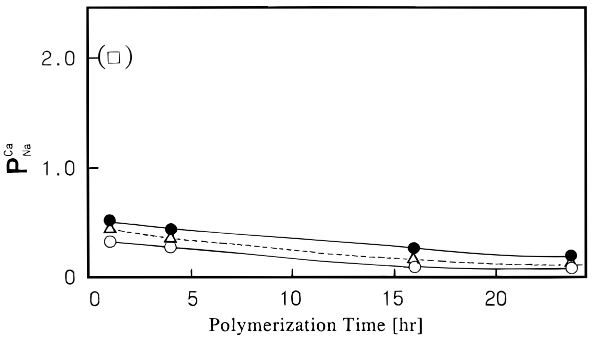


Figure 6. The change in $P_{Na}{}^{Ca}$ for the composite membrane (NEOSEPTA CM-1 and polypyrrole) versus polymerization time. ○: the polypyrrole layer facing the anode compartment; ●: the polypyrrole layer facing the cathode compartment (the membrane was equilibrated in a 1.0 N HCl solution before equilibration in the mixed salt solution); △: the polypyrrole layer facing the anode compartment (the membrane was equilibrated in a 0.5 N ammonia solution before equilibration in the mixed salt solution); □: without the layer.

solution abruptly increased for the membrane with a 24 h polymerization time. Though the reason is not clear, polypyrrole, a rigid and tight polymer, grew into the inner part of the membrane and might restrict migration of the larger calcium cations. We concluded that an increase in the electrical resistance of the membrane was not very remarkable after considering the formation of the polypyrrole layer under suitable conditions.

Figure 6 shows the relative transport number between the calcium ions and sodium ions when the polypyrrole layer of the cation exchange membrane faced the desalting side (anode compartment) and the layer faced the concentrated side (cathode side). The membrane used in this case was equilibrated with a 1.0 N hydrochloric acid solution before immersing the membrane in a mixed salt solution. When the layer faced the anode compartment, the $P_{Na}{}^{Ca}$ decreased from 2.05 (without the layer) to 0.11−0.24. At the same time, when the layer faced the cathode compartment, the $P_{Na}{}^{Ca}$ was also remarkably decreased.

It was expected that the polypyrrole on the membrane surface acts as a rejection layer for the calcium ions when the calcium ions permeate through the cation exchange membrane. It is well-known that when a thin cationic polyelectrolyte layer is formed on the desalting side of the cation exchange membrane, monovalent cations permeate selectively through the cation exchange membrane during electrodialysis.[19] It is thought that since the polypyrrole layer on the membrane surface has secondary amino groups and the membrane was immersed in the hydrochloric acid solution before equilibration with the mixed salt solution, a cationically charged layer was formed on the desalting side of the membrane. Namely, a decrease in the permeation of calcium ions might be due to the difference in the electrostatic repulsion force of the cationic charge on the membrane surface against the calcium ions and sodium ions. After the same membrane had been equilibrated with a 0.5 N ammonia solution to depress the dissociation of the secondary amino groups and then equilibrated with a mixed salt solution, the relative transport number was measured. The values for the $P_{Na}{}^{Ca}$ are also low, but slightly higher than those for the membrane equilibrated with the hydrochloric acid solution, as shown in Figure 6 (dotted line; facing the layer to the anode compartment). Though the secondary amino groups of the polypyrrole layer might be partially protonated during the immersion of a mixed salt solution of calcium chloride and sodium chloride after immersion in an ammonia solution, it is thought that electrostatic repulsion was not the main driving force behind the decrease in the permselectivity of calcium ions. To confirm the existence of the cationic charge in the polypyrrole layer, the current efficiency was measured by first passing current from the polypyrrole layer side and then from the opposite side after equilibration in a 1.0 N hydrochloric acid solution. Figure 7 shows the change in current efficiency for both cases versus polymerization time. The measurement of the current efficiency from the polypyrrole layer to the anode side was the same as the value for a membrane without a polypyrrole layer. It was still about 3−5% lower than when the current was passed from the opposite side and independent of the polymerization time. Apparently, chloride ions leaked through the cation exchange membrane due to the existence of a layer on the cathode side. It has been reported that when a cationic polyelectrolyte is adsorbed on the concentrated side (cathode side) of a cation exchange membrane, the current efficiency decreases.[20] Therefore, this proves that the polypyrrole layer acted as a thin anion exchange membrane and did not increase as an anion exchange membrane with an increase in polymerization time.

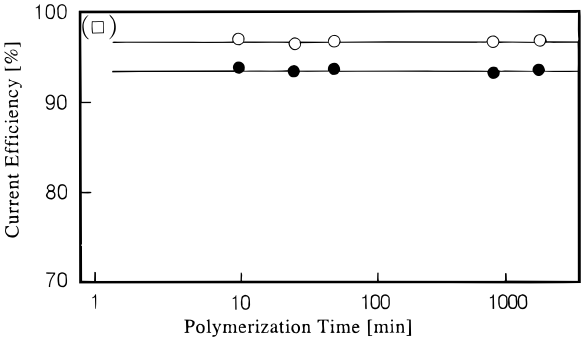


Figure 7. The change in current efficiency for the composite membrane (NEOSEPTA CM-1 and polypyrrole) versus polymerization time. ○: polypyrrole layer facing the anode compartment; ●: polypyrrole layer facing the cathode compartment. The membrane was equilibrated in a 1.0 N HCl solution before equilibration in a mixed salt solution; □: without the layer.

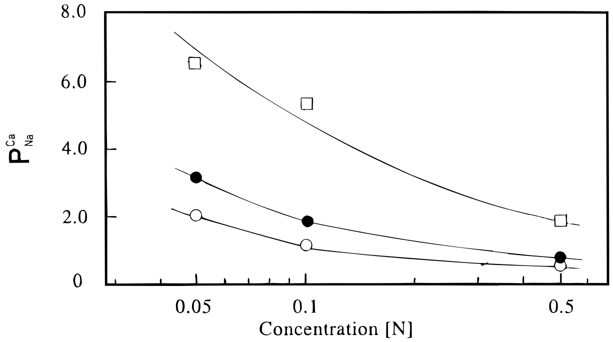


Figure 8. The change in $P_{Na}{}^{Ca}$ of the composite membrane (NEOSEPTA CM-1 and polypyrrole, polymerization time: 4 h) versus the concentration of the mixed salt solution. ○: polypyrrole layer facing the anode compartment; ●: polypyrrole layer facing the cathode compartment; □: NEOSEPTA CM-1. The membrane was equilibrated in a 1.0 N HCl solution before equilibration in a mixed salt solution.

Figure 8 shows the change in the $P_{Na}{}^{Ca}$ for the cation exchange membrane with and without the polypyrrole layer versus the concentration of the mixed salt solution.

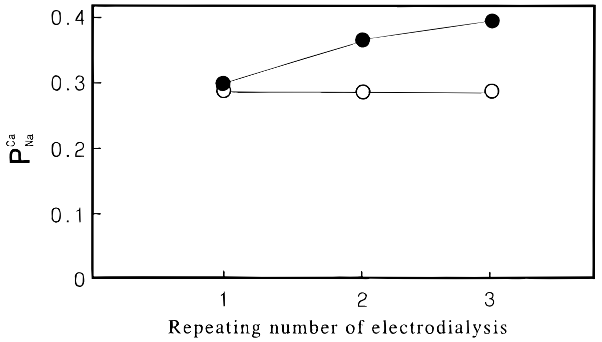


Figure 9. The change in $P_{Na}{}^{Ca}$ of the composite membrane (NEOSEPTA CM-1 and polypyrrole; polymerization time: 4 h) by repeated electrodialysis. ○: polypyrrole layer facing the anode compartment; ●: polypyrrole layer facing the cathode compartment. The membrane was equilibrated with a 1.0 N HCl solution before equilibration in a mixed salt solution.

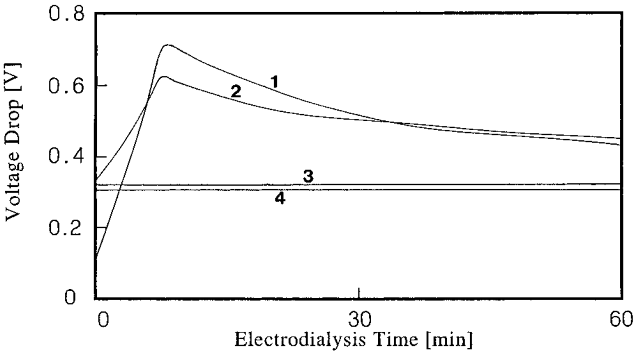


Figure 10. The change in the voltage drop across the composite membrane (NEOSEPTA CM-1 and polypyrrole, polymerization time: 10 min) during electrodialysis. 1: first electrodialysis with the polypyrrole layer facing the cathode compartment; 2: second electrodialysis with the polypyrrole layer facing the cathode compartment; 3: first electrodialysis with the polypyrrole layer facing the anode compartment; 4: second electrodialysis with the polypyrrole layer facing the anode compartment.

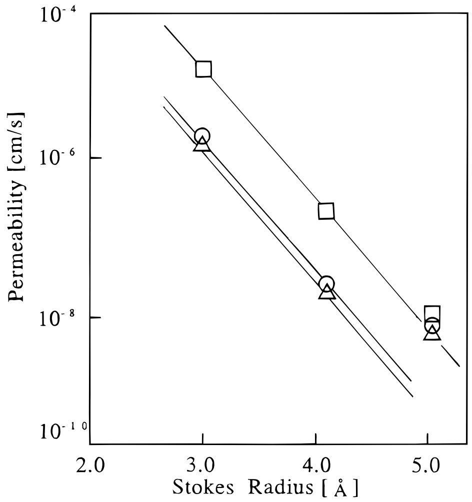


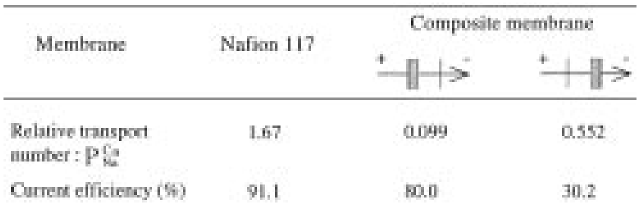
Figure 11. The relationship between the permeability coefficient of neutral molecules through the composite membrane (NEOSEPTA CM-1 and polypyrrole; polymerization time: 10 min) and their Stokes radius. □: without the layer (NEOSEPTA CM-1); ○: polypyrrole layer facing the dilute compartment; △: polypyrrole layer facing the concentrated compartment.

Though the $P_{Na}{}^{Ca}$ of the cation exchange membrane without the layer naturally increased with decreasing concentration of the solution, the $P_{Na}{}^{Ca}$ of the composite membrane was extremely low, being almost independent of the orientation of the layer to the anode or the cathode compartment (though $P_{Na}{}^{Ca}$ was slightly low when the layer faced the anode side). Though it is understandable that the $P_{Na}{}^{Ca}$ decreased during electrodialysis when facing the layer to the desalting side due to rejection of calcium ions on the membrane surface, it is unusual for $P_{Na}{}^{Ca}$ to decrease when it faced the concentrated side. To clarify this phenomenon, the electrodialysis with the layer facing the same direction was repeated three times. Though the $P_{Na}{}^{Ca}$ was constant when the layer faced the anode side, the value increased with the increasing number of electrodialyses when faced in the opposite direction (Figure 9). This suggests that the calcium ions accumulated on the cation exchange membrane due to the difficulty in permeating through the layer on the concentrated side. Figure 10 shows the change in voltage drop at the membrane during electrodialysis when the polypyrrole layer faced the anode compartment or the cathode compartments. Though the voltage drop at the membrane was constant during the electrodialysis when the layer faced the anode side, the voltage drop increased during electrodialysis, attained a maximum, and decreased gradually when facing the opposite direction. It is thought that when calcium ions enter into the membrane, the ions cannot permeate through the membrane and a breakthrough would only occur after a sufficient accumulation of calcium ions in the membrane at some level. In fact, when the electrodialysis was repeated, the second voltage drop was lower than the first one when the layer faced the anode compartment. When the layer faced the cathode side, a high voltage at the beginning of electrodialysis was observed (the electrical resistance for the calcium ion form membrane is about 6 times higher than that for the sodium ion form as shown in Figure 5).

3. Evaluation of the Change in Pore Size for the Cation Exchange Membranes. It was reported that the composite membrane composed of the anion exchange membrane and polypyrrole showed properties of high acid retention when a hydrochloric acid solution was concentrated during electrodialysis.[11] One of the reasons is due to a sieving effect resulting from the rigidity of the polypyrrole itself. It is postulated, based on Figures 9 and 10, that the sieving of calcium ions by the polypyrrole layer contributed markedly to the decrease in $P_{Na}{}^{Ca}$. Figure 11 shows the relationship between the permeability coefficient of neutral molecules through the membranes and the Stokes radius of the molecules. The permeability coefficients of urea and glucose decreased one-tenth after the formation of a polypyrrole layer on the membrane surface when the layer faced either the concentrated or the diluted sides, but especially the concentrated side. This means that the small pores of the membrane were clogged by the layer. The permeability coefficient of saccharose was almost the same value as the membrane without the layer. This means that most of the large pores of the membrane, which are a small percentage, remained after the formation of the polypyrrole layer.

The methods used to give monovalent cation permselectivity to the cation exchange membrane, which have been reported, are to form a highly cross-linked layer on the membrane surface (a coating of a polycondensation polymer composed of phenol, sodium phenol sulfonate, and formaldehyde, in which the content of phenol was high),[21] the formation of a thin cationically charged layer on the desalting side of the cation

Table 2. Relative Transport Number and Current Efficiency of Composite Membrane from Nafion 117 and Polypyrrole[a]



Membrane	Nafion 117	Composite membrane	
		+ −	+ −
Relative transport number : P_{Na}^{Ca}	1.67	0.099	0.552
Current efficiency (%)	91.1	80.0	30.2

[a] Polymerization time: 24 h.

exchange membrane, and the introduction of specific cation exchange groups, which strongly interact with multivalent cations, in the membrane. It was reported that a monovalent cation permselective exchange membrane with a cationic polyelectrolyte layer does not show a remarkable decrease in the permeability coefficient of neutral molecules and the electrical resistance of the membrane does not increase during electrodialysis when the layer exists on the concentration side.[22] To further confirm the cationic charge in the polypyrrole layer, a different composite membrane was prepared using a perfluorocarbon sulfonic acid membrane and pyrrole. The electrodialytic properties of the composite membrane are shown in Table 2. When the layer faced the anode compartment, the $P_{Na}{}^{Ca}$ decreased remarkably. On the other hand, when the current was passed from the opposite direction, the cation exchange membrane changed into an anion exchange membrane (current efficiency was only 30.2%). This proves that the polypyrrole layer is anion-exchangeable. However, when the polypyrrole layer of the membrane faced the anode side in electrodialysis (using the composite membrane as bipolar ion exchange membrane), a considerable change in the pH of the solution in both compartments was not observed.

Conclusions

Pyrrole was polymerized by the ferric ions ion-exchanged with the sulfonic acid groups of the cation exchange membrane, and a polypyrrole layer was formed on one surface of the membrane. Subsequently, the cation exchange membrane, an insulator, changed in electrical conductor (membrane surface). It was also confirmed that the ferric ions in the membrane were reduced to the ferrous ions after the polymerization.

The decrease in the $P_{Na}{}^{Ca}$ of the cation exchange membrane with a polypyrrole layer is remarkable. One reason for this phenomenon is due to a sieving effect for the calcium ions by the polypyrrole layer because the layer, located on the concentrated side of the membrane, also restricted the permeation of calcium ions. The pore size of the membrane is also decreased by the presence of this layer. At the same time, a cationic charge exists in the polypyrrole layer, resulting in a decrease in the current efficiency during electrodialysis when facing the cathode side. From these results, the difficulty in the permeation of calcium ions through the composite membrane is due to the synergistic effect of the sieving of calcium ions and difference in the electrostatic repulsion for calcium and sodium ions.

Figure 12 shows the change in the relative transport number of alkali earth metal cations to sodium ions by the formation of the polypyrrole layer. The relative transport number of the alkali earth metal cations together with the calcium ions was also remarkably decreased. This is a new method to obtain a monovalent cation permselective membrane during electrodialysis.

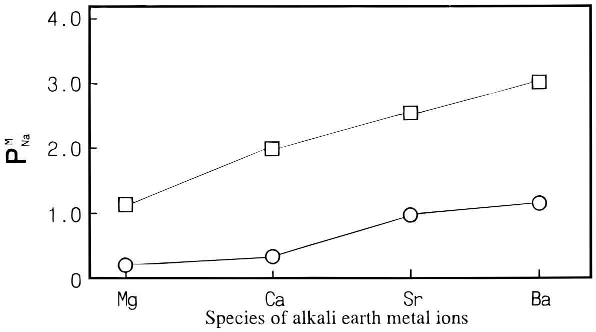


Figure 12. The relative transport number between alkali earth metal cations and sodium ions of the composite membrane (NEOSEPTA CM-1 and polypyrrole, polymerization time: 4 h). ○: composite membrane (facing the layer to the anode compartment); □: without the layer.

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