Effects of Applied Potentials on Permselectivity of Ions through Polypyrrole/Porous-Polypropylene Composite Membrane

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ABSTRACT: A composite membrane was prepared by the combination of polypyrrole with a porous-polypropylene film, and its permselectivity was investigated. The permeability and selectivity of various sodium salts through the membrane were changed with an applied potential. The permeation of anions at the positive potentials was due to the migration through the positive sites of the polypyrrole layer, as well as the diffusion from the difference of concentration and potential. The contribution of the migration effect to the anion permeation was very large. The main factors dominating the permeation character of different anion species were the size and valence of the anions. The composite membrane worked effectively as a functional separation membrane to control the ionic permeability by potential application. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 647–653, 1998

Key words: polypyrrole; porous polypropylene; composite membrane; permselectivity; separation control with potentials

INTRODUCTION

Conducting polymers have been receiving much attention as novel functional materials because they have various electronic and electrochemical properties that the usual organic polymers never have. A lot of conducting polymers with a variety of chemical structures have been developed so far. Nevertheless, the polymers that are as highly conductive as metals and that are maintained for long periods under the usual atmosphere have not been obtained. Because most conducting polymers become highly conductive by the addition of "dopants" (electron donors or electron acceptors), the dopants are readily inserted into and eliminated from the polymer chains (the so-called chemical doping and dedoping) accompanying the oxidation and reduction of the polymer by various external stimuli.[1–5] Besides the conductivity, the electrochemical, electromagnetic, optical, and spectral properties of conducting polymers are also extensively changed by the doping–dedoping process. Hence, conducting polymers are not suitable for uses as simple electrical conductors at the present, and their utility as practical industrial materials have been investigated for applying the property changes by the doping–dedoping processes. For example, changes of their chemical potentials are applied to materials for batteries,[6] changes of their optical properties are applied to materials for displays,[7] and changes of their electrical and magnetic properties are applied to materials for sensors[8] and memories.[9] In addition, changes of their electrochemical properties are proposed for their application to novel functional separation membranes that can dynamically control the ionic permeability by an external operation like applying potential. However, there are only a few reports[10–17] on the ionic permeation

and separation with conducting polymer membranes. There are also insufficient studies on the ionic permeation and separation mechanisms of conducting polymer membranes under applied potentials.

From these viewpoints we prepared a separation membrane combined with a typical conducting polymer of polypyrrole (PPy) and a porous material of polypropylene, and we investigated the changes of permselectivity of a variety of ions through the membrane with different potentials applied in order to clarify the effectiveness of the functional separation membranes to control the ionic permeability by applying potential. We report the results and discuss the permeation and separation mechanisms of the composite membrane in this work.

EXPERIMENTAL

Materials

Guaranteed grades of pyrrole and acetonitrile were purified before use by reduced pressure or simple distillation. Cellguard 2400 (CG2400), which is an unwoven cloth produced by Hoechst with a 0.2-μm maximum pore size and a circa 20-μm thickness, was used as the porous-polypropylene material to prepare a composite membrane with PPy. The other reagents were all of guaranteed grade and were used without further purification.

Preparation of PPy/CG2400 Composite Membrane

The PPy/CG2400 composite membrane was prepared through the procedure shown in Figure 1. CG2400 was first made conductive by a sputtering of gold on the one side at 1.2 kV and 5 mA for 1 h with a Jeol JFC-1100 fine coater. The distance between the CG2400 surface and the Au target was 6 cm. An amount of 4.15 cm^2 of this membrane as a working electrode and a Pt wire as a counterelectrode were immersed in 0.5M pyrrole-acetonitrile solution with 0.1M (C$_2$H$_5$)$_4$NClO$_4$ as a supporting electrolyte. The Au-sputtered side of the working electrode was set in the opposite direction to the counterelectrode. The pyrrole was polymerized electrochemically by applying a constant cathodic current density of 1.0 mA/cm^2 with an Advantest TR6142 dc voltage and current generator for 30 min at 25°C. The formed polypyrrole grew in the pores of CG2400, resulting in a PPy/
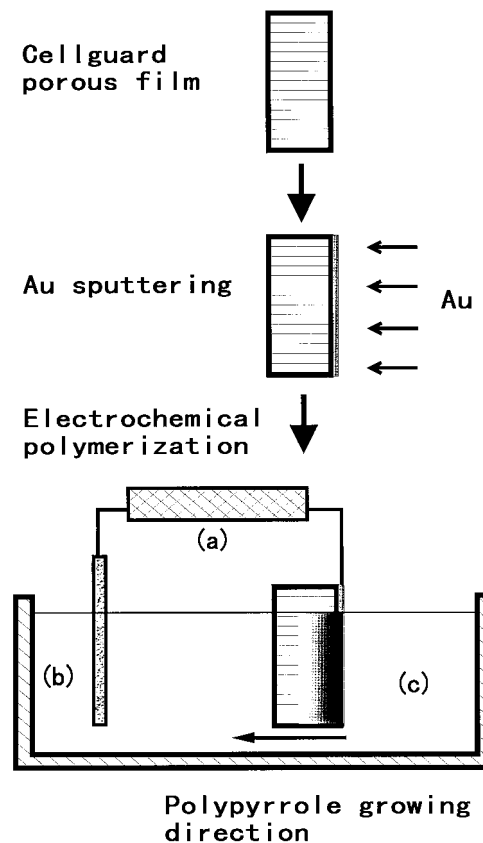

Figure 1 Preparation of a polypyrrole/Cellguard 2400 composite membrane (PPy/CG2400): (a) galvanostat, (b) Pt counterelectrode, and (c) 0.5M pyrrole + 0.1M (C$_2$H$_5$)$_4$NClO$_4$ acetonitrile solution.

CG2400 composite membrane. The composite membrane was rinsed repeatedly with methanol and distilled water for removal of the residual reagents.

Measurements

The morphology of PPy/CG2400 was investigated with a scanning electron microscope (Jeol JSM-T5800LVC) and compared with the results for the Au-sputtered CG2400.

The ion permeation character of PPy/CG2400 was estimated by the value of the ion permeability and its changes by applying potential. The ion permeability was measured at 25°C with an electrochemical cell shown in Figure 2. After immersion for one night in the aqueous solution containing 0.0001M of the electrolyte to be measured, PPy/CG2400 was put between two glass cells. One cell (cell A) was filled with 0.1M of the electrolyte (28.45 mL). The other (cell B) was filled
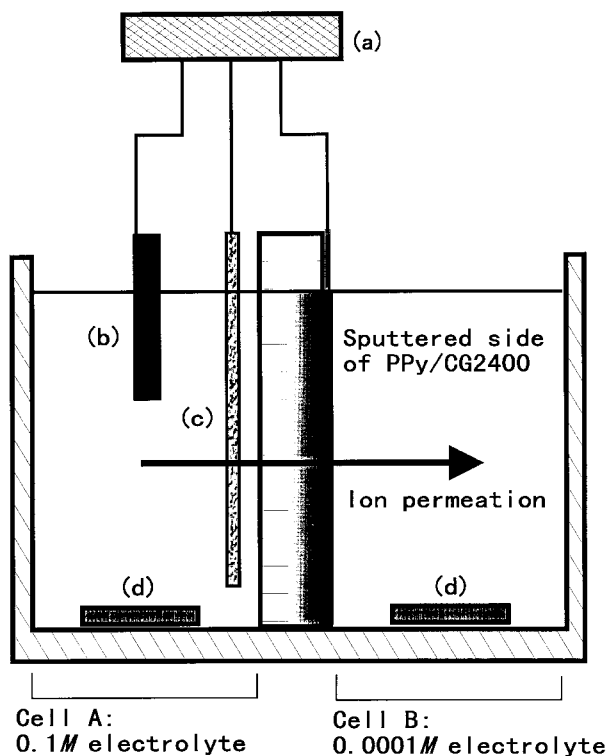
Figure 2 Electrochemical cell with PPy/CG2400 for measurements of ion permeability: (a) potentiostat, (b) satulated calomel electrode, (c) Pt counterelectrode, and (d) stirrer.

with 0.0001M of the electrolyte (24.70 mL) attached to the Au-sputtered side of the PPy/CG2400. Then the Pt wire counterelectrode and a saturated calomel electrode as a reference were set in cell A and attached to a potentiostat (Hokuto HA-501G) with a function generator (Hokuto HB-104) together with the PPy/CG2400 as the working electrode. In order to exchange the residual electrolytes contained in the as-prepared PPy/CG2400 with the electrolyte to be measured, the potential was cycled 100 times at 20 mV/s between -0.4 and $+0.4$ V under a constant stirring condition, and the electrolyte solutions in both cells were replaced with fresh ones before measurement. After this pretreatment, PPy/CG2400 was kept at a fixed potential for 30 min and the electrolyte solutions in both cells were refreshed again. Then the concentration of the electrolyte ions in the cells was measured after applying the potential for 1 h. This procedure was repeated subsequently from -0.4 to $+0.4$ V. The electrolytes used for the measurements were sodium salts of monovalent (NaCl, NaClO$_3$, CH$_3$COONa, sodium benzoate) and divalent

(Na$_2$SO$_4$, sodium malonate) anions. The concentrations of the anion species and the sodium ion were measured by ion chromatography and atomic absorption spectroscopy, respectively. The ion permeability through PPy/CG2400 was calculated from the results above by the standard steady-state Fickian diffusion model[14]:

$$\text{flux} = (DK/\chi) \cdot \Delta C$$

where D is the diffusion coefficient of the transport species (ions) across the membrane of thickness χ, K is the partition coefficient for the transport species between the solution phase and the membrane, ΔC is the concentration difference between the source solution (cell A) and the receiver solution (cell B), and the product DK is the permeability.

RESULTS AND DISCUSSION

Morphology

Scanning electron micrographs of PPy/CG2400 were measured for investigation of the morphology. Figure 3 shows the micrographs of the cross section and the Au-sputtered surface of PPy/CG2400 (below) together with those of the Au-sputtered CG2400 (above). The right side of the cross sections is the Au-sputtered surface, and the layer on the right edge is adhesive tape to vertically fix the samples on a holder. As shown in the micrographs of PPy/CG2400, PPy particles grew from the Au-sputtered side to the counterelectrode through the inside of the CG2400 and the surface of the Au-sputtered side was covered with the particles packed in the pores of the CG2400.

Ion Permeability

The ion permeability through PPy/CG2400 was measured for various sodium salt electrolytes under applied potential. As an example of the results, changes in the permeability of the Na$^+$ and Cl$^-$ of NaCl with an applied potential are shown in Figure 4. The permeability of Cl$^-$ increased as the applied potential was raised while that of Na$^+$ decreased. According to Figure 5, PPy has a neutral polymer backbone in the reduced state and applying an anodic potential results in the oxidized state backbone with positive charges accompanying the incorporation of electrolyte anions, which is known as "electrochemical doping." From
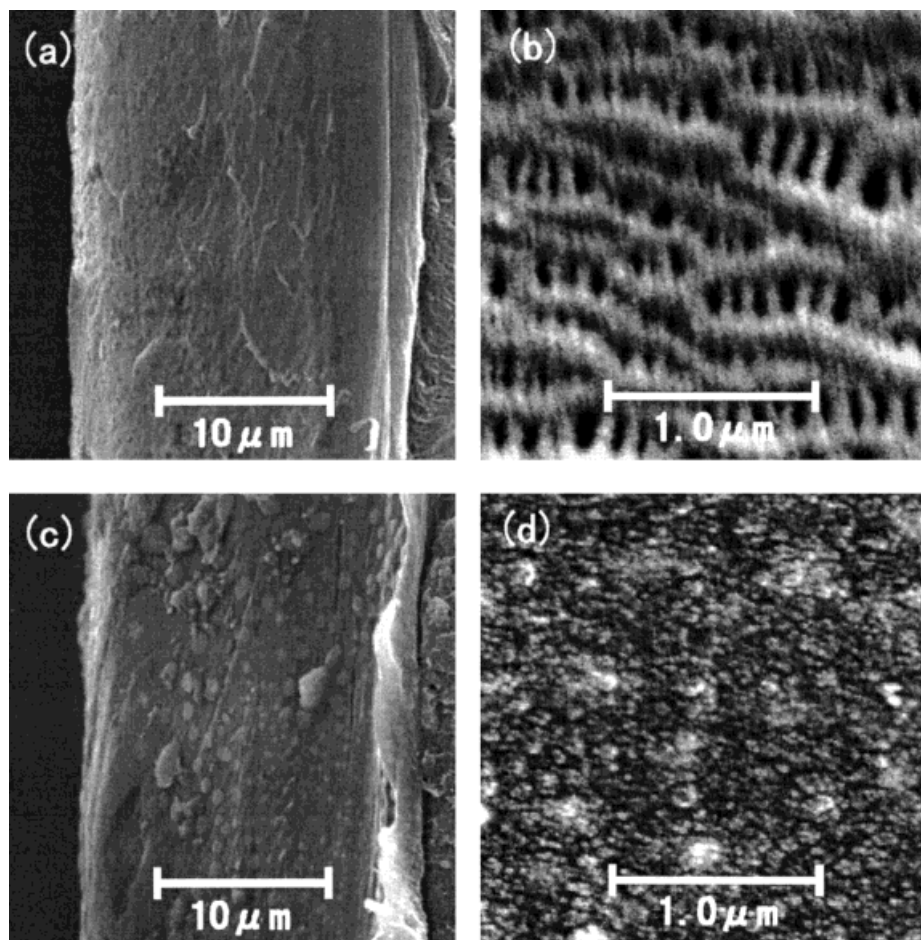
Figure 3 Scanning electron micrographic analysis of CG2400 and PPy/CG2400: (a) cross section of CG2400 (the right side is the Au-sputtered surface), (b) Au-sputtered surface of CG2400, (c) cross section of PPy/CG2400 (the right side is the Au-sputtered surface), and (d) Au-sputtered surface of PPy/CG2400.

this viewpoint, PPy film is regarded as an ion-exchange membrane in which the number of anion exchange groups is varied with an applied potential. In the present measurement, cations are apt to permeate through PPy/CG2400 at negative applied potentials while anions are apt to permeate through PPy/CG2400 at positive potentials because the highly conductive Au layer on PPy/CG2400 is located in the permeate side. In addition to the potential effect, the anions permeating at the positive potentials are likely to undergo a static interaction with the increased positive charges of the PPy layer. Hence, the permeation of cations at the negative potentials is due to the diffusion that is derived from the difference of concentration and potential between the feed side (cell A) and the permeation side (cell B), and permeation of anions at positive potentials is due

to the migration through the positive sites of the PPy layer, as well as the diffusion. Cl^- is more advantageous to the diffusion than Na^+ because the effective radius[18] (at 25°C) of the hydrated ions of the former is smaller than the latter (Cl^-, 3 Å; Na^+, 4 Å). Nevertheless, the permeability of Cl^- at the positive potentials was much lower than that of Na^+ at the negative potentials as shown in Figure 4. This suggests that the contribution of the migration effect to the anion permeation is very large. Paulse and Pickup[11] reported similar results on chronoamperometric studies of PPy film. Figure 6 shows changes in permeability of the Na^+ and CH_3COO^- of CH_3COONa with an applied potential. The permeability of anions increased as the potential was raised while that of cations decreased in similar to NaCl. However, their permeability, especially of the CH_3COO^-
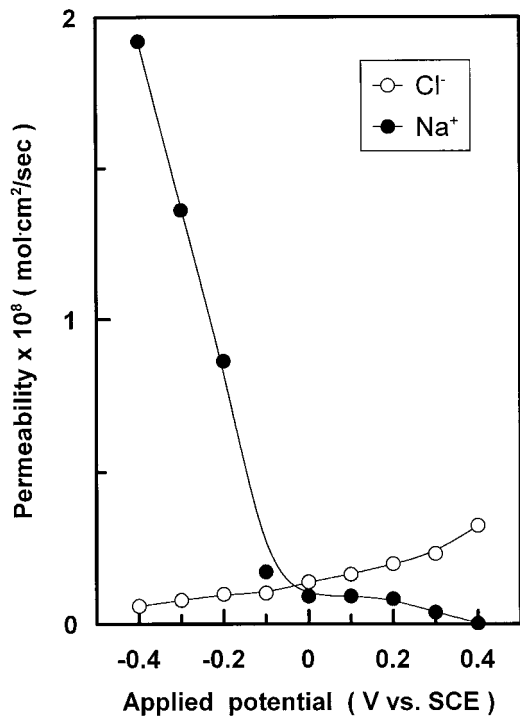
Figure 4 Changes in ion permeability of NaCl through PPy/CG2400 with an applied potential.
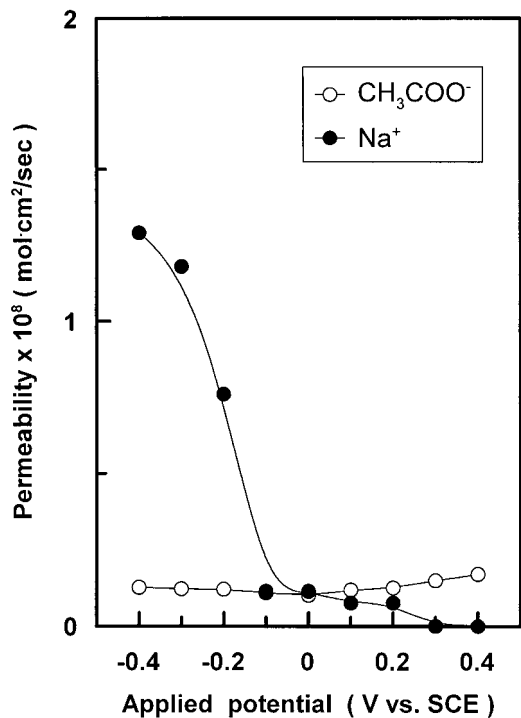

Figure 6 Changes in ion permeability of CH₃COONa through PPy/CG2400 with an applied potential.

anion, was lower than that of NaCl. The extent of the permeability changes with potential was also lower. These differences in permeation characteristics between different electrolytes were originated from the PPy layer because they were not found for the Au-sputtered CG2400.

Figure 7 shows changes in anion permeability of a variety of sodium salts through PPy/CG2400 with an applied potential. The permeability and its dependency on potential differed largely according to the species of anion. The different permeation characteristics were considered to be mainly due to the migration rate of anions through the PPy layer. In order to define the cause of the different migration rate, the permeability of the anions at a reduction potential (-0.4 V), a neutral potential (0.0 V), and an oxidation potential ($+0.4$ V) were plotted against the ion
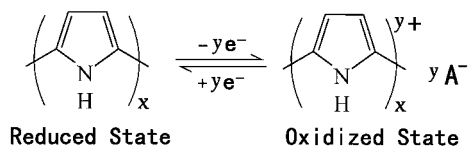

Figure 5 Electrochemical redox mechanism of polypyrrole. A⁻, electrolyte anion.

radius of the anions in Figure 8. It was found that the permeability increased as the radius and valence of the anions decreased at the neutral and oxidation potentials. At the reduction potential the permeability change was similar to that at the neutral potential when the ion radius was sufficiently high, but it decreased when the "ion radius" (the effective radius of the hydrated ions) became too much lower (below ca. 4.5 Å). It is considered that these results were caused by the fact that the mobility of the anions through the PPy layer was higher as the radius was lower and that some portions of the anions with sufficiently lower radius moved to the counterelectrode against the concentration difference at the reduction potential. It is also considered that the static interaction between the anions and the positively charged PPy layer was stronger in decreasing the migration rate when the ionic valence was higher. If the morphology of the PPy layer was not changed by the electrochemical oxidation process accompanying the doping with different anion species, it can be concluded that the factors dominating the permeation character of the anions were the size and valence of the anion species. However, some workers[12] reported morphological changes of PPy membrane by polarization, al-
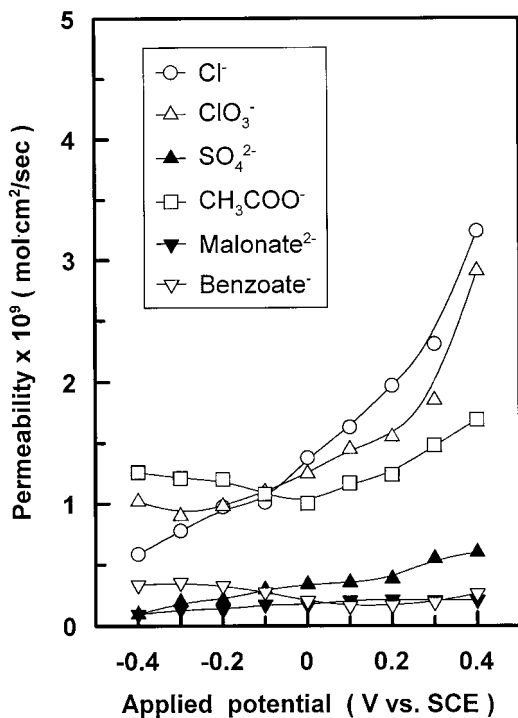
Figure 7 Changes in anion permeability of a variety of sodium salts through PPy/CG2400 with an applied potential.
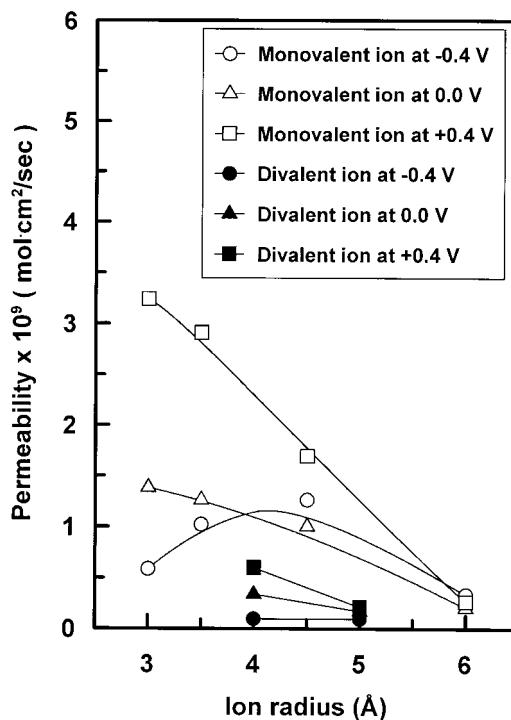

Figure 8 Effect of ion radius on anion permeability through a PPy/CG2400 with an applied potential.

though the effects of the different dopant anion species on the morphological changes have not been investigated in detail. Further investigations are necessary for the elucidation of a more detailed mechanism of the ionic permselectivity of PPy/CG2400.

Figure 9 shows the effect of ion radius on the ratio of anion permeability at +0.4 and −0.4 V. It was found that the ratio was higher as the radius was lower and the valence of the anions was higher. That is, the permeability of the anions with lower ion radius and higher valence is controlled to a larger extent by applying potential.

Selective Separation from Anion Mixtures

When the ion permselectivity of PPy/CG2400 described in the previous section was considered, it was expected that some specific anions would be separated selectively from different anion mixtures. In order to confirm this, an ion permeation experiment was carried out with an aqueous solution containing $0.1M$ NaCl and $0.1M$ CH_3COONa as examples of different anion mixtures. Figure 10 shows the changes in permeability of each anion in the
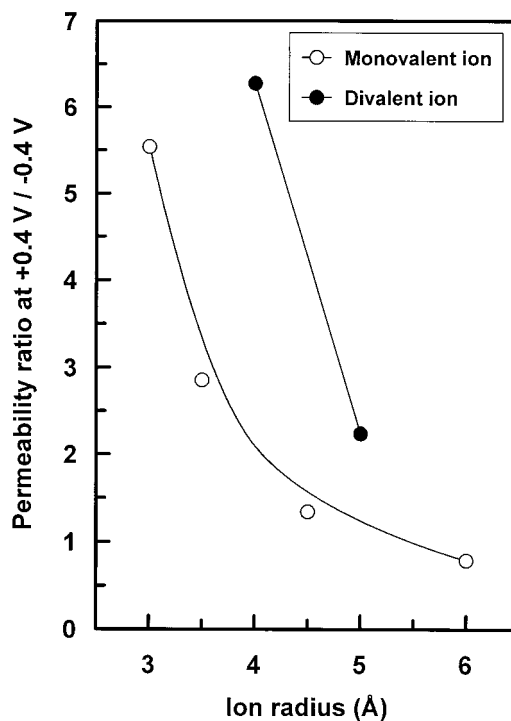

Figure 9 Effect of ion radius on the ratio of anion permeability at +0.4 and −0.4 V.
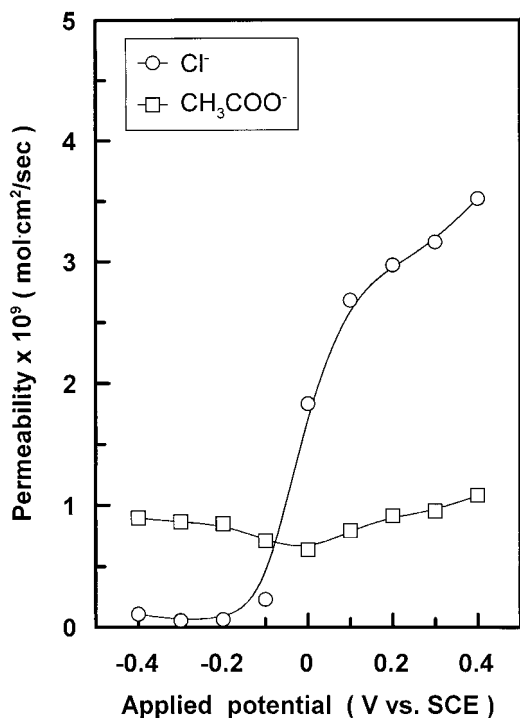
Figure 10 Changes in permeability of each anion in an NaCl/CH$_3$COONa mixed solution through PPy/ CG2400 with a potential applied.

NaCl/CH$_3$COONa mixed solution through PPy/ CG2400 with an applied potential. The figure shows that the permeability of Cl$^-$ was lower than that of CH$_3$COO$^-$ below circa -0.1 V. As the potential was raised, it increased faster and was much higher than that of CH$_3$COO$^-$ at positive potentials. Hence, PPy/CG2400 works as a functional membrane that not only separates different anion species but also controls their separation ratio by the applied potentials. The extent of the permeability changes of Cl$^-$ for this mixed solution was larger than that for an NaCl single solution that was shown in Figure 4. This was thought to be caused by a preferential permeation of Cl$^-$, which was relatively enhanced by the positive charges of the PPy layer compensated by the negative charges of the CH$_3$COO$^-$ anions migrating more slowly.

CONCLUSION

PPy/CG2400 was shown to work effectively as a functional separation membrane to control ionic permeability by applying potential, and the factors dominating their permeation character are the size and valence of the ion species. This work

investigated its permselectivity for only some electrolyte ions with low molecular weight. However, we expect that the potential-controllable permselectivity of PPy/CG2400 will be applied to other useful industrial materials with higher molecular weights when the effects of the preparation conditions on the morphology of the resulting polymer films are investigated in detail. The morphology of conducting polymer films like PPy films can be changed largely by a variety of polymerization conditions,[19] and the size effects of ion species dominating the permeation character are concerned with the morphology of the membrane.

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