diameter. This orientation allows for the metal halide bonds in adjacent Pc layers to align in an opposed fashion. This model does not address the orientation of the Pc's in the first layer (halide up or halide down), and does not rule out the possibility that the first layer of Pc will adopt a slightly different attitude with respect to the surface plane than subsequent deposited layers. Present RHEED technologies do not have sufficient resolution in measuring the spacing between diffraction streaks for these large molecules to discriminate such subtle effects, however, studies in progress promise that additional structural information can be obtained by refinements in the technology.

Previous studies of vanadylphthalocyanine have tried to demonstrate the correlation between stacking of the adjacent Pc's and the visible absorbance spectra of thin films of such materials.[23] It has been suggested that the slipped stacking pattern like that of Figure 6b will lead to a red-shifted absorbance maximum. To our knowledge however, there have been no studies of true single-crystal thin film Pc's where a strict comparison of the absorbance spectrum and the crystallographic orientation has been done.

The optical data of Figure 5 demonstrate that the Pc multilayer formed must be nearly homogeneous, as indicated by the narrowness of the major abosrbance peak. The origin of the shoulder on the blue side of this absorbance peak is not clear, but since its intensity with respect to the major peak is constant over a wide range of Pc film thicknesses, it suggests that it arises from the same type of vibronic coupling seen in the solution monomer absorbance spectra.[13-15] It is clear that a complete structural analysis of such thin Pc layers will be necessary in order to fully assign these spectral features.

It appears possible now, however, to grow organic thin films, with thicknesses necessary for reasonable linear and nonlinear optical characterization, by the MBE approach.[10] The combination of metal dichalcogenide formation on transparent substrates, and the ordered growth of the subsequent organic layer, may allow for the formation of organic layers with high optical density, with narrow excitonic bands in a desirable wavelength range, which lead to interesting new studies in the areas of photoconduction, optical switching, and optical data storage.

Acknowledgment. We gratefully acknowledge support for this research from the National Science Foundation and the Materials characterization Program—State of Arizona. We are also grateful to Bruce Parkinson and Fumio Ohuchi for the samples of bulk SnS_2 and for several helpful discussions throughout the course of these studies.

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Properties of Ion-Exchange Membranes Combined Anisotropically with Conducting Polymers. 2. Relationship of Electrical Potential Generation to Preparation Conditions of Composite Membranes

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Preparation and properties of cation-exchange membranes with which polypyrrole had been combined anisotropically were studied in detail. When one side of a cation-exchange membrane in the ferric ion form contacted an aqueous pyrrole solution for a given period, pyrrole polymerized easily and quickly and formed a polypyrrole layer in the membrane matrix beginning from the membrane surface. The polypyrrole layer was so tight that pyrrole molecules could not permeate it in 50 h of exposure. X-ray microanalysis of a cross section of the membrane revealed its anisotropic structure. During this oxidative polymerization of pyrrole, more than 90% of the ferric ions in the membrane phase were reduced to ferrous ions. On the surface of the membrane opposite the polypyrrole layer was a cation-exchange membrane layer that contained ferric ions, while most of the membrane contained ferrous ions. When this composite membrane was held tightly between two platinum plates, a electrical potential was observed because of Fe^{2+}–Fe^{3+} redox reactions. To confirm this further, a ferric ion form of a cation-exchange membrane and a cation-exchange membrane in which polypyrrole had been impregnated from both surfaces were clamped together tightly between two platinum plates and placed into pure water to hydrate the membranes. A higher electrical potential was observed when compared with the composite membrane.

Introduction

Polypyrrole, polyaniline, other conducting polymers, and their analogues have been widely studied in the field of pure and applied materials chemistry.[1-5] Examples of their possible applications include batteries,[6-11] electrochromic displays,[12-14] solid electrolytic capacitors,[15] etc. I

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Table I. Characteristics of Cation-Exchange Membranes Used

	Neosepta CM-1[a]	Neosepta CH-45T[a]	Nafion 117[b]
backing	poly(vinyl chloride)	poly(vinyl chloride)	
thickness, mm	0.16	0.16	0.175
electric resist,[c] Ω cm^2	1.1	2.3	3.5
transport no.[d]	>0.98	>0.98	>0.95
ion-exchange capacity[e]	2.38	2.11	0.92
water content[f]	0.38	0.38	0.22

[a] Sulfonated styrene–divinylbenzene copolymer type. [b] Perfluorocarbon sulfonic acid type. [c] Equilibrated with 0.5 N NaCl solution, measured with 1000 cycle a.c. at 25.0 °C. [d] Measured by electrodialysis of 0.5 N NaCl solution; current density 20 mA/cm^2, at 25 °C. [e] Mequiv/g of Na$^+$ form dry membrane. [f] Equilibrated with 0.5 N NaCl solution (g of H_2O/g of Na$^+$ form dry membrane).

reported in a previous paper[16] that a composite anisotropic membrane could be produced by contacting one side of a ferric ion form of a cation-exchange membrane with an aqueous pyrrole solution. The membrane was anisotropic because pyrrole polymerized on the membrane surface quickly and formed a tightly structured polypyrrole layer that additional pyrrole molecules could not permeate easily. When this composite membrane was held tightly between two platinum plates, an electrical potential was observed. The potential was dependent on relative humidity. This was a new and interesting functional material from various perspectives. Therefore, the effect of preparation conditions of the composite membrane on the potential generation was examined in this work.

Experimental Section

Materials. Ion-Exchange Membranes. Commercial cation-exchange membranes, Neosepta CM-1 and CH-45T, which are made by Tokuyama Soda Co., Ltd., and Nafion 117 made by du Pont de Nemours Inc. were used. Table I shows characteristics of Neosepta CM-1 and CH-45T and Nafion 117. Before use, Neosepta was alternatively equilibrated with 0.5 N sodium chloride solution and 1.0 N hydrochloric acid solution and then equilibrated with an aqueous 0.173 M ferric chloride (or 0.2 N cupric chloride) solution. Nafion was boiled in pure water for at least 60 min after immersion in 60% nitric acid for 7 days at room temperature and then equilibrated in the 0.173 N ferric chloride solution. Before the composite membrane was produced, the starting membrane was washed with pure water to remove excess salt.

Chemicals. Pyrrole, $FeCl_3 \cdot 6H_2O$, and $CuSO_4 \cdot 5H_2O$ were obtained from Wako Pure Chemicals Ind. and used without further purification. Deionized water was used in all experiments.

Preparation of Composite Membrane. A two-compartment cell (effective membrane area 9.0 cm × 9.0 cm; capacity of each compartment 243 cm^3) was used to produce the anisotropic structure membrane. After a cation-exchange membrane of ferric (cupric) ion form had been installed in the two-compartment cell, one compartment was filled with an aqueous 0.745 M pyrrole solution and the other with pure water. After this was stirred for a given period (from 30 min to 50 h), the membrane was taken out from the cell, washed with pure water to remove nonpolymerized pyrrole, and dried under nitrogen.

To produce a membrane in which polypyrrole exists more homogeneously, a cation-exchange membrane, Neosepta CH-45T, of ferric ion form was immersed in the pyrrole solution for 4 h. This membrane was also washed with pure water and dried under nitrogen. All composite membranes were stored under dry nitrogen atmosphere. All experiments were carried out at room temperature.

Measurement of Potential. The electrical potential of the composite membrane was measured by clamping a 1.0 cm^2 (1.0 cm × 1.0 cm) piece of the composite membrane tightly between two platinum plates, each connected directly to an *X–t* recorder (Toa Electronics Co., Ltd. EPR-231A; internal resistance 2 MΩ). In this measurement, a Zero Shunt Ammeter (Hokuto Denko Ltd., HM-103) was connected in series in order to measure the current passing through the composite membrane. The potential without load was measured by an electrometer (Hokuto Denko Ltd., HE-104). The polypyrrole side was negative, and the cation-exchange membrane layer was positive. The potential was measured in a desiccator in atmosphere of different humidity. After the composite membrane with electrodes had been put into the desiccator filled with air, the relative humidity in the desiccator was decreased below 2% and then the relative humidity was increased. Most of the potential measurements were carried out by cycling dry and wet conditions alternatively several times. Pure water in a Petri dish was placed in the desiccator to raise the humidity, and P_2O_5 was used to lower humidity. Relative humidity was measured with a Humidex YH-12 (Yamato Engineering Co., Ltd.).

When a composite membrane in which polypyrrole had been impregnated from both sides of the membrane and a ferric ion form of a cation-exchange membrane were clamped together between two platinum plates to measure the potential, the membranes and electrodes were exposed to wet and dry conditions in the same manner. Though a potential of about 50 mV was observed at relative humidity more than 80%, the response of the potential was too slow. Therefore, the cell containing this membrane assembly was immersed in pure water for subsequent potential measurements.

Measurement of the Cross Section of the Composite Membrane. The composite membrane sample for the cross section was washed with a 1.0 N hydrochloric acid solution several times to remove ferric ions, equilibrated with an aqueous 1.0 N hydrogen bromide solution, and dried under vacuum. Cross sections of the composite membrane were observed through an X-ray microanalyzer (JXA-8600M, JEOL) by measuring the intensity of emitted Br$^-$ X-rays. The distribution of polypyrrole over the cross section of the membrane was interpreted to be the distribution of ion-exchanged bromide ions.

Analysis of Ferric and Ferrous Ions in the Composite Membrane. The membranes stored under dry nitrogen atmosphere were immersed in an aqueous 0.5 N sodium chloride solution under stirring several times to elute iron ions from the membranes. Collected solutions were divided into two parts. 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 ferric ions to the ferrous; then 1,10-phenanthroline was added to that solution too. The concentration of ferrous–1,10-phenanthroline complex (maximum absorption peak 510 nm)[17] was determined by a U-3400 Hitachi spectrophotometer. The concentration of ferric ions was calculated to be the difference between total iron ions and ferrous ions.

Results and Discussion

Preparation of Membranes with an Anisotropic Structure. It was reported in the previous paper that an anisotropic membrane was produced from a ferric ion form of a cation-exchange membrane and an aqueous pyrrole solution.[16] Pyrrole molecules diffusing into the cation-exchange membrane were oxidized to form polypyrrole in the membrane matrix by ferric ions that ion-exchanged

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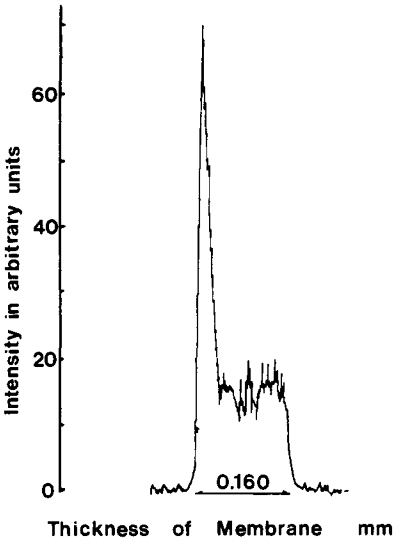

Figure 1. X-ray microanalysis of a cross section of Neosepta CM-1 combined with polypyrrole (2-h polymerization). The membrane was equilibrated with an aqueous hydrogen bromide solution.

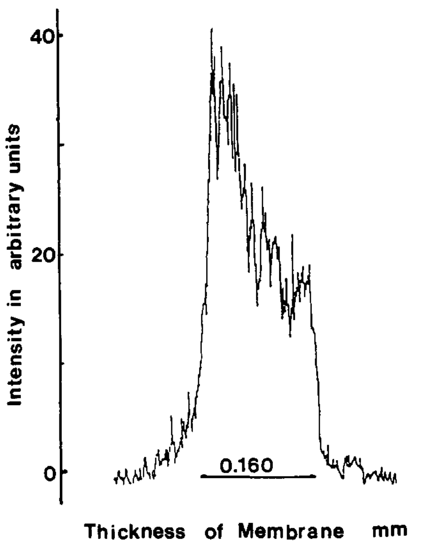

Figure 2. X-ray microanalysis of a cross section of Neosepta CM-1 combined with polypyrrole (4-h polymerization). The membrane was equilibrated with an aqueous hydrogen bromide solution.

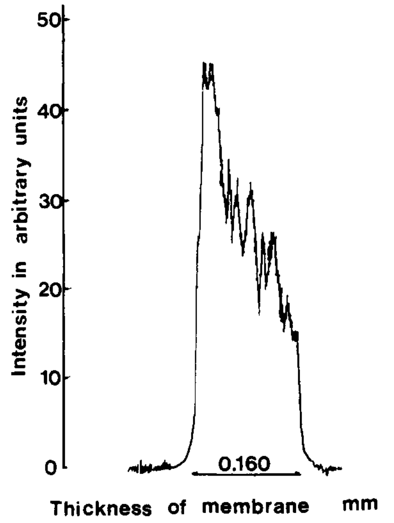

Figure 3. X-ray microanalysis of a cross section of Neosepta CM-1 combined with polypyrrole (50-h polymerization). The membrane was equilibrated with an aqueous hydrogen bromide solution.

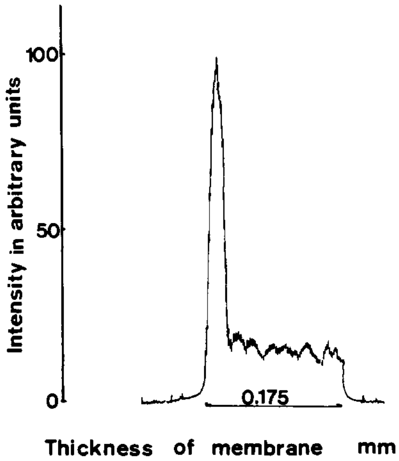

Figure 4. X-ray microanalysis of a cross section of Nafion 117 combined with polypyrrole (6.5-h polymerization). The membrane was equilibrated with an aqueous hydrogen bromide solution.

with the membrane. The anisotropy of the membrane was evident when cross sections of the membranes were examined by X-ray microanalysis. Figures 1–3 show results of the X-ray microanalysis of Neosepta CM-1 when the polymerization period was 2, 4, and 50 h. In the case of the 2-h polymerization membrane, a distinct polypyrrole layer was observed on the membrane surface. Neosepta membrane contains poly(vinyl chloride) as a component of the membrane. As pyrrole has a good affinity[18] for poly(vinyl chloride), the Neosepta membrane swelled markedly with an aqueous pyrrole solution. Nevertheless, the anisotropy of the membrane was maintained even when one side of the membrane contacted the pyrrole solution for 50 h. When Figure 2 is compared with Figure 3, there is no remarkable difference. This suggests that the polymerization of pyrrole does not proceed through the entire membrane thickness. Figure 4 shows the cross section of the Nafion membrane when the polymerization period was 6.5 h. A more distinct polypyrrole layer was formed on Nafion than on Neosepta CM-1. It is concluded that the polypyrrole layer that had been formed on the membrane surface prevented further growth of the layer because the layer was so tight that even pyrrole molecules could not permeate it.

Relationship between Electric Potential and Polymerization Conditions. It was reported in the previous paper that potential is generated from Fe^{2+}–Fe^{3+} redox reactions on a cation-exchange membrane layer and a polypyrrole layer of the composite membrane.[16] Also since the polypyrrole layer acts as an anion-exchange membrane, the composite membrane is a kind of bipolar ion-exchange membrane. However, the membrane potential of the bipolar membrane is of opposite polarity to that observed for these composite membranes.

Figure 5 shows a typical example of relationship between potential and relative humidity. (The polymerization period was 4 h.) Though a dry composite membrane did not show any potential, the potential increased abruptly with increasing relative humidity, showing a maximum and decreasing with further increase of the humidity. When the membrane was subsequently dried, the potential showed a small peak and then decreased. This suggests that there is a humidity value that causes partial hydration

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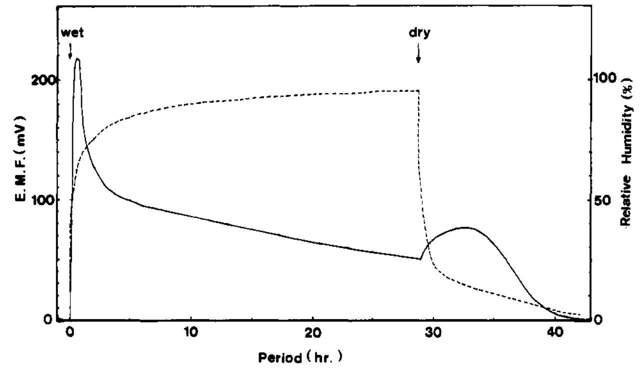

Figure 5. Typical example of change in electric potential of a composite membrane with changing relative humidity: (1) electric potential measured with a 2-MΩ load; (2) composite membrane produced by contacting one side of ferric ion form Neosepta CM-1 with an aqueous pyrrole solution for 4 h; (3) solid line shows the potential and dotted line shows relative humidity.

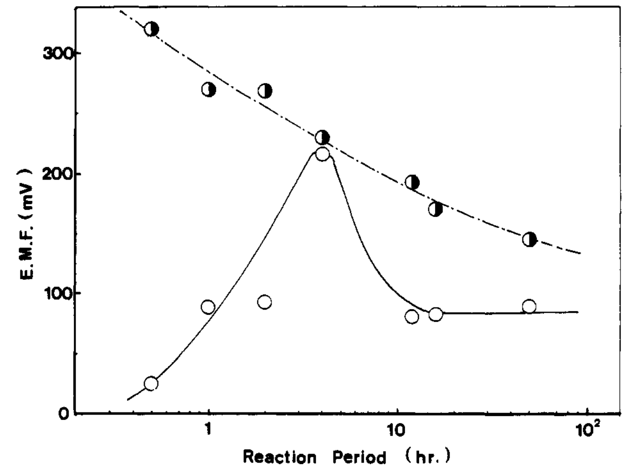

Figure 6. Relationship of maximum electric potential of composite membrane to polymerization period. (◑) Electric potential measured by electrometer after equilibration with an atmosphere of relative humidity of 55–60% for 12 h. (○) Maximum value of electric potential measured with a 2-MΩ load.

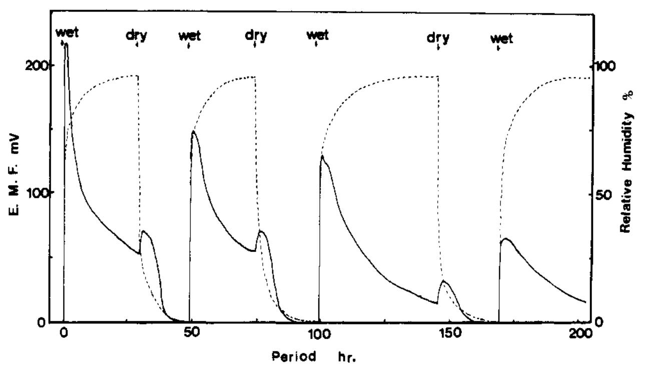

Figure 7. Change in electric potential of a composite membrane (Neosepta CM-1, 4-h polymerization) with changing relative humidity (load resistance 2 MΩ). Solid line shows electric potential and dotted line shows relative humidity.

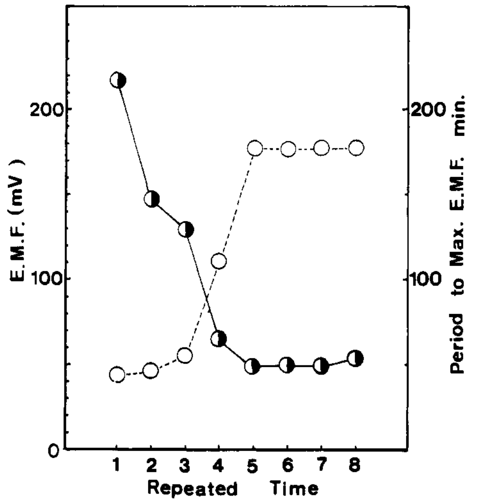

Figure 8. Change in maximum value of electric potential and period to attain the maximum electric potential with repeating dry–wet cycles. (◑) Maximum value of electric potential in a wet–dry cycle. (○) Period to attain the maximum potential. The composite membrane of 4-h polymerization was used.

and generates the highest potential. The potential generated from Fe^{2+}–Fe^{3+} redox reactions is cancelled by the membrane potential of the bipolar membrane with full hydration in the high-humidity range. In general, although hydration and dehydration of polymers are relatively slow, the moisture content of ion-exchange membranes changes rapidly because of the presence of ion-exchange groups. As mentioned in the Experimental Section, an increase or decrease of relative humidity was controlled by vaporization of water or dehumidification by P_2O_5. When moisture control was carried out by air saturated with water and dry air, the potential increased and decreased very quickly.

Since the polymerization period was shown to affect the structure of polypyrrole layer on the membrane surface (Figures 1–3), it follows that the polymerization period ought to affect the potential generated by the composite membrane as it hydrates. Figure 6 shows the relationship between potential and polymerization period. The potential measured by an electrometer (without discharge) decreased with increasing polymerization period. When the polymerization period was short, a distinct thin polypyrrole layer that contains ferrous ions exists on the ferric ion form of the membrane. It is thought that ferrous and ferric ions coexist in the cation-exchange membrane layer with increasing ferrous ion content during the polymerization period. Since the thickness of the ferric ion form of the layer decreased with increasing polymerization period, the potential might be expected to decrease gradually. However, the potential with a 2-MΩ load shows a maximum value at 4 h of polymerization. In this case, when the amount of ferrous ions is balanced with that of ferric ions, the potential ought to show a maximum value because the cell discharged with a 2-MΩ load. It is thought that 4-h polymerization is such a point. The concentration of reactive ferric ions was richer than that of ferrous ions before 4-h polymerization and vice versa after 4-h polymerization. Wet–dry cycles were repeated several times by using the composite membrane of 4-h polymerization. The result is shown in Figure 7. Although the maximum potential decreased with increasing cycles (the potential of the first cycle was 217 mV and that of fouth cycle 65 mV), the maximum potential after fifth cycle attained an almost constant value, not decreased in further wet–dry cycles as is shown in Figure 8. The period to attain the maximum potential also increased in the initial few cycles and attained a constant value. This also suggests that there were both ferric ion layers and ferrous ion layers at the starting time of discharge. Figure 9 shows the relationship between the potential and relative humidity of the composite membrane of 50-h polymerization in which there was no decrease in potential with repeated wet–dry cycles. This means that there were both ferric and ferrous ions in the cation-exchange membrane layer under equilibrium conditions. The period to attain the maximum value of the potential was longer than that of 4-h polymerization.

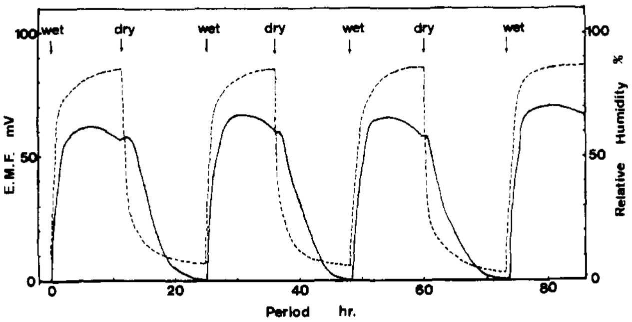

Figure 9. Change in electric potential of a composite membrane (Neosepta CM-1, 50-h polymerization) with changing relative humidity (load resistance 2 MΩ). Solid line shows electric potential and dotted line shows relative humidity.

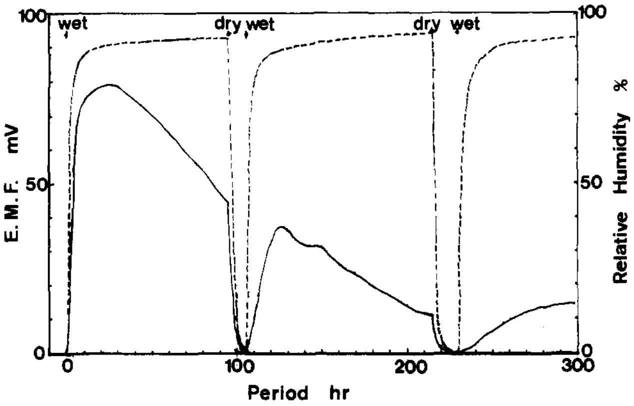

Figure 10. Change in electrical potential of a composite membrane polymerized by cupric sulfate (Neosepta CM-1, 4-h polymerization) with changing relative humidity (load resistance 2 MΩ). Solid line shows electric potential and dotted line shows relative humidity.

Table II. Increase in Membrane Weight by Polymerization of Pyrrole with Cupric Ions and Ferric Ions[a]

oxidant	Fe^{3+}		Cu^{2+}	
polymerization period, h	1	6	1	6
wt increase,[b] %	5.4	6.5	3.9	5.1

[a] After ferric ion form or cupric ion form of Neosepta CM-1 had been immersed in an aqueous pyrrole solution for 1 and 6 h, the membrane was washed with methanol and equilibrated with pure water. [b] (Dry weight of composite membrane − dry weight of NEOSEPTA CM-1/dry weight of NEOSEPTA CM-1) × 100.

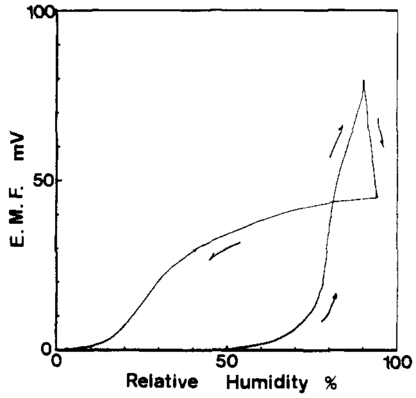

Figure 11. Change in electrical potential of a composite membrane polymerized by cupric sulfate with relative humidity. A dry membrane was exposed to moist conditions, and then relative humidity decreased.

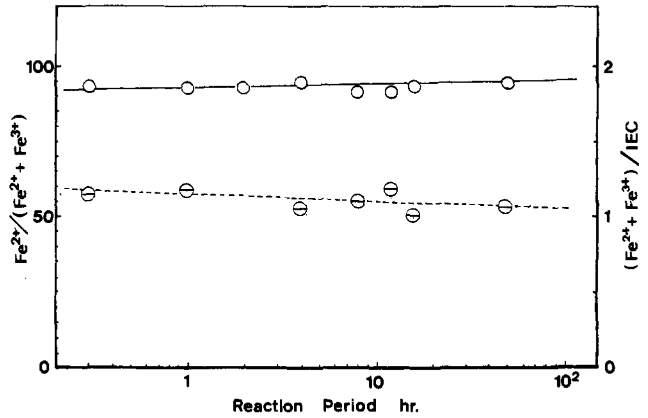

Figure 12. Relationship of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ and $(Fe^{2+} + Fe^{3+})$/(ion-exchange capacity) to polymerization period. Solid line shows a molar ratio of ferrous ions to total iron ions and dotted line shows equivalent ratio of total iron ions to ion exchange capacity. (1) Iron ions eluted from the membranes by immersing the membranes in 0.5 N NaCl for 4 h with stirring, and the same procedure was repeated. (2) Ferrous ions analyzed by spectrophotometric method of ferrous ion–1,10-phenanthroline complex.

There are many redox agents able to initiate pyrrole polymerization. For example the cupric–cuprous reduction should also polymerize pyrrole. To demonstrate this, Neosepta CM-1 was equilibrated with an aqueous cupric sulfate solution, and one side of the membrane was contacted with an aqueous pyrrole solution. When cupric ion form of the membrane was used in the polymerization, the color of the membrane (light brown) began to change in black with lapse of more than 15 min after immersing the membrane into the aqueous pyrrole solution. On the contrary, ferric ion form of the membrane began to change to black within 0.5 min under the same conditions. Table II shows the weight gain of the membranes with the polymerization by ferric ions and cupric ions. Apparently the weight increase of the ferric ion form of the membrane was larger than that of the cupric ion form at the initial stage of the polymerization. Although polymerization speed was slow compared with ferric ions, a membrane with similar anisotropic structure was obtained. Figure 10 shows the change in potential due to changing the relative humidity for a membrane polymerized with cupric ions for 4 h. As was the case with ferric form of the membranes, the cupric form produced the highest potential when the polymerization period was 4 h. It is not clear that the period to show the highest potential of the cupric form agreed with that of the ferric form because the polymerization speed of the cupric form was slow compared with the ferric form. Although there were some differences, i.e., the maximum value of the potential and shape of discharge curves (there were no small peaks after drying), between Figures 7 and 10, similar phenomena were observed in both cases. Figure 11 shows the relationship between the potential and relative humidity. Retardation of hydration and dehydration of the composite membrane was reflected by the hysteresis in the changes in the potential with relative humidity. (Similar phenomena were also reported in the composite membranes produced by ferric ions.[16])

Ionic Composition in the Membrane Phase. To examine the ratio of ferrous ions to ferric ions in the membrane phase, iron ions in membranes of various polymerization periods were analyzed. Figure 12 shows molar ratios of ferrous ions to total iron ions (sum of ferrous and ferric ions) and the equivalent ratio of total iron ions to ion-exchange capacity of the membrane. Unexpectedly, more than 90% of iron ions in the membrane were ferrous ions. Before the membrane contacted the aqueous pyrrole solution, the membrane was equilibrated with an aqueous ferric chloride solution. And after polymerization of

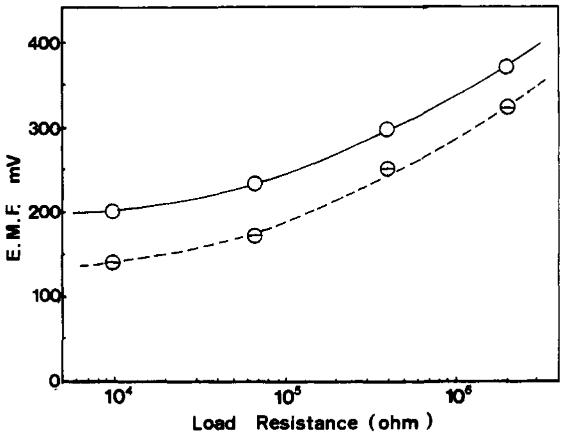

Figure 13. Relationship of electrical potential to load resistance for assembly of two membranes (ferric ion form Neosepta CH-45T and polypyrrole-impregnated Neosepta CH-45T). (○) Potential of the starting time of discharge. (⊖) Potential after 10-h discharge. (1) Polypyrrole-impregnated Neosepta CH-45T produced by immersing ferric ion form Neosepta CH-45T into an aqueous pyrrole solution for 4 h to polymerize pyrrole from both sides of the membrane. (2) After ferric ion form Neosepta CH-45T and polypyrrole-impregnated Neosepta CH-45T (2.0 cm × 2.0 cm) were clamped between platinum plates, the membranes and electrodes were put into pure water.

pyrrole, the equivalent ratio of iron ions to ion-exchange capacity was almost unity. This means that iron ions were released from the membrane during the polymerization to balance the charge of the membrane.

On the other hand, since most of the iron was present as ferrous ions in the membrane, it seems that the residual ferric ions change in ferrous ions completely during wet–dry cycles and then the potential attains zero. However, the potential was observed even after eighth cycles of dry–wet cycles as is shown in Figure 8. The potential after fifth cycles of Figure 8, which attained a constant value, almost agreed with the potential of Figure 9, in which the membrane contained the least amount of ferric ions. This might be because ferrous ions produced by reduction on the surface of the cation-exchange membrane layer were oxidized by oxygen in the air during dry conditions. To confirm this, one cell was dried in a desiccator filled with air and the other was dried in a desiccator filled with nitrogen by using the composite membrane of 50-h polymerization. The potential of the composite membrane dried in air did not decrease, but that of the membrane dried in nitrogen decreased every wet–dry cycle.

Confirmation of Redox Reactions Using Model Membranes. To conclude that potential generation is based on Fe^{2+}–Fe^{3+} redox reactions and to confirm a role of polypyrrole layer in potential–humidity characteristics, the following experiments were carried out: (1) a ferrous ion form of the cation-exchange membrane was prepared with a ferric ion layer by oxidizing one surface of the ferrous ion membrane and measuring the potential generated. (Neosepta CM-1 was equilibrated with 1 N hydrochloric acid and then 0.250 M ferrous chloride solution in an atmosphere of nitrogen. This ferrous-ion-form membrane was placed in a cell where it was exposed to nitrogen gas on one side and air on the other side for 3 h to produce a gradation in the oxidation of iron.) (2) The potential generated by separate Neosepta CM-1 membranes in ferrous and ferric forms clamped together between platinum plates was examined. (3) The potential generated by separate membranes composed of a ferric ion membrane and a composite membrane in which polypyrrole was impregnated from both sides of membrane was studied. In the first experiment, no potential was recorded in the *X–t* recorder when this controlled membrane was tested in the humidity apparatus, but a potential of 42 mV was measured when it was placed in pure water. In the second experiment, when the separate membranes plus electrodes were immersed in water, a potential of 172 mV was observed, but the potential declined abruptly and reached 50 mV in 10 h. This is because of rapid ion-exchange reactions. In contrast, a polypyrrole composite membrane produced by Neosepta CH-45T and a ferric ion form Neosepta CH-45T tested in the same way had an initial potential of 372 mV and the potential only declined to 330 mV in 10 h. Figure 13 shows the relationship between potential and load resistance. Apparently, a Fe^{2+}–Fe^{3+} redox cell was formed.

The results of above-mentioned experiments are consistent with the result reported in the previous paper,[16] in which the ratio of ferrous ions to the ferric changed after discharge. In fact, for example, a transparent cation-exchange membrane such as Nafion changed from pale yellow (ferric ion form) to colorless after discharge. The polypyrrole layer appears to contribute to the potential–humidity relationship through formation and stabilization of ferrous ions in the composite membrane and by providing an electron-transfer medium for the $Fe^{2+} + e^- \rightarrow Fe^{3+}$ reaction.

In conclusion it is noted that pyrrole polymerized easily and quickly in the ferric ion form cation-exchange membrane to form a very tight layer that imparts interesting and potentially useful properties to cation-exchange membranes.

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Registry No. NeSEPTA CM-1, 107721-14-2; CH-45T, 66796-30-3; Nafion 117, 67577-82-6; ferric chloride, 7705-08-0; polypyrrole (homopolymer), 30604-81-0; cupric sulfate, 7758-98-7.