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Effect of polymer materials on membrane potential, rectification and water splitting in bipolar membranes

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Bipolar membranes are of practical interest in a new process for the commercial production of acids and bases. In this study, the effect of polymer components and structure on membrane potential, rectification and water splitting in bipolar membranes was discussed. The experimental results for the membrane potential agree well with the theoretical predictions if the effective charge densities of bipolar membranes were assumed to be 0.0001 times smaller than those which were estimated for each layer separately. The results of the water splitting and rectification effects show that a membrane exhibiting a high rectification effect has a low water splitting effect. The water splitting ability depends on the thickness of the anion exchange layer. Though it has been pointed out that the state of the intermediate boundary region is also responsible for water splitting, the results indicate that the chemical composition of the anion exchange layer plays an important role. If the membrane structure is similar to an ionomer, the water splitting is also more effective. It is very important to prevent water swelling as far as possible, not only by polymer crosslinking but also by supporting the membrane with woven cloth. Copyright © 1996 Elsevier Science Ltd.

(Keywords: bipolar membranes; membrane potential; rectification)

INTRODUCTION

A bipolar membrane is a layered structure involving a cation-selective membrane joined to an anion-selective one. It is well known that such membranes show a rectification effect as seen in semiconductor p–n junctions[1–3]. The transport phenomena of ions across such membranes have been studied since 1911[4] whereas they were first developed in the 1950s[5,6]. In recent years they have become of practical interest in a new process for the commercial production of acids and bases[7–10]. However, many problems have to be solved before realizing full industrial production with the application of bipolar membranes. Water splitting has to be accompanied by water dissociation into hydrogen and hydroxide ions at the boundary surface between anionic and cationic layers and successive ion diffusion through charged layers. Therefore it is necessary to discuss separately both the phenomena of water dissociation and diffusion of dissociated ions. Problems in ion diffusion can be analysed by using the same framework as that of a monopolar ion exchange membrane, because it is possible for anion and cation exchange layers to be prepared individually. The discussion of water dissociation is much more difficult, since it is impossible to extend the intermediate region from a membrane.

Ohki predicted the rectification effect by consideration of the Donnan equilibrium and the Nernst–Planck equation[11]. It was strongly affected by the fixed charge densities in the cation and anion exchange layers. However, the water splitting effect cannot be explained from his theory. Mafé *et al.* explained water splitting using also the Donnan effect and the Nernst–Planck equation. A water molecule dissociates into a cation (H^+) and an anion (OH^-) obeying the second Wien effect[12–14]. It was suggested that the effect of water splitting had to be controlled by the dielectric constant at the boundary surface. On the other hand, Simons *et al.* have suggested that the water splitting takes place by chemical reaction on the primary, secondary or tertiary amine in the anion exchange layer[15–17]. Therefore, comparing experimental data on different kinds of bipolar membrane is one of the methods to elucidate these problems.

In this study, various types of bipolar membranes that have different polymer materials, polymer structures, fixed charge groups, thickness and fixed charge densities were prepared. From the measurement of the membrane potential, the pH change under constant applied voltage and the rectification, the effects of polymer components

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and structure on water splitting in bipolar membranes were discussed.

EXPERIMENTAL

Samples

Three types of membranes were prepared: hydrocarbon type, perfluorocarbon type and sandwich type.

Hydrocarbon type[18]. For the preparation of the anion exchange layer, a dimethylformamide (DMF) solution of poly(styrene) and poly(chloromethylstyrene) (Asahi Chemicals)—into which *N,N,N′,N′*-tetramethyl-1,6-diaminohexane was added in order to introduce positively charged groups of quaternary amine—was stirred for 1 min, then cast on a glass plate surrounded by a rectangular frame (13 cm × 10 cm) of about 1 mm thickness and allowed to dry at 125°C for 10 min in the air. Subsequently, a DMF solution of sulfonated poly(butadiene-*co*-styrene) rubber (Asahi Chemicals) was cast quickly on the top surface of the anion exchange layer surrounded by the rectangular frame and allowed to dry at 125°C for 6 min in the air for the preparation of the cation exchange layer. The glass plate was cooled down to room temperature and soaked in 0.1 mol dm^{-3} aqueous solution of potassium chloride to peel off the membrane. Thus a bipolar membrane was obtained. Swelling by water is prevented by polymer crosslinking. It is assumed that charged groups are distributed homogeneously, and an intermediate region between the anion and cation exchange layers is very clear, without a thin water layer. Four kinds of bipolar membranes with different thicknesses were prepared and are listed in *Table 1*. The membrane thickness was controlled by the thickness of the rectangular frame. An anion exchange layer and a cation exchange layer were also prepared separately in the same format as above to determine the charge density of each layer by membrane potential measurements, respectively.

Perfluorocarbon type. We were provided with the bipolar membrane (B-17), which consisted of perfluorocarbon, by Toso Co. Ltd[19]. The anion exchange layer is composed of quaternary and secondary amines, and the cation one of sulfonic acid groups. The structure of this polymer is similar to an ionomer (that is Nafion) where charged groups are concentrated in small pores or channels. Perfluorocarbon is hydrophobic and sorbed water can be stored only near fixed charge groups. Since the fixed charge density is defined as the number of charged groups per water volume in a membrane, it will be estimated as about 30 times larger than that of the hydrocarbon type membrane. An intermediate region, where the charged group changes from negative to positive, has not been observed clearly.

Sandwich type. An anion exchange membrane that is composed of quarternary amine groups (A-101, Asahi Chemicals) and a cation exchange membrane composed of sulfonic acid groups (K-101, Asahi Chemicals) were superposed together. The main polymer composition of both membranes is similar to that of the hydrocarbon type membrane as cited previously. However, this membrane is supported by woven cloth in order to prevent further water swelling. It is supposed that the intermediate region is a very thin water layer. The thickness and fixed charge density of each membrane are shown in *Table 1*.

Membrane potential measurements

Two compartments separated by a membrane were filled with potassium chloride solutions at the same concentration in order to measure the potential using an Ion-Meter (IM-40S, TOA) connected with a pair of glass electrodes (HS-205C, TOA). The concentration was varied from 10^{-4} to 1 mol dm^{-3}, and the reference electrode was installed in the compartment facing the negatively charged layer. All measurements were carried out at 25°C. Before reaching the steady state, the membrane potential was measured as a function of time. First it decreased and finally a constant value was obtained after 15 h.

In order to investigate the influence of a boundary surface region, another measurement on the membrane potential was introduced as shown in *Figure 1*. In addition to the two external compartments, an intermediate compartment was installed between an anion exchange membrane (A-101) and a cation exchange membrane (K-101). Both of the external compartments were filled with potassium chloride solutions with the same concentration. During the membrane potential measurement, the salt concentration ratio of an external to the intermediate compartment was kept constant. The other experimental conditions were the same as those cited above.

Membrane potential was also measured in the monopolar state which keeping the concentration on one side constant at 10^{-3} mol dm^{-3} and changing it on the other

Table 1 Thickness and fixed charge density of membranes

	Cation exchange layer		Anion exchange layer	
	Thickness (μm)	Charge density (mol dm^{-3})	Thickness (μm)	Charge density (mol dm^{-3})
Sample A	75	0.65	75	0.92
Sample B	37	0.65	37	0.92
Sample C	75	0.65	37	0.92
Sample D	37	0.65	75	0.92
B-17[a]	90	20	90	4.7[a]
K-101	120	0.68		
A-101			140	0.58

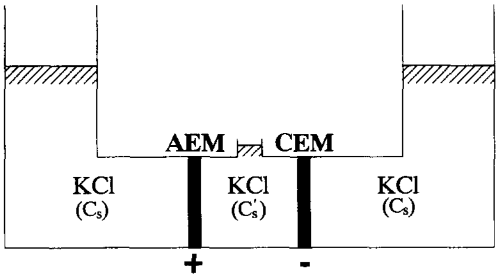
[a] By titration method

side from 10^{-4} to $1\,\mathrm{mol\,dm^{-3}}$ in order to determine the fixed charge density of each charged layer.

pH change under constant applied voltage

The measurements of pH change caused by water splitting were carried out using a laboratory-scale cell designed for the production of acids and bases. The cell was composed of four compartments as shown in *Figure 2*. The two outside compartments (R_2, L_2) were separated by an anion or a cation exchange membrane with an effective area (A_m) of $8\,\mathrm{cm^2}$, respectively. They were maintained by circulation of $0.5\,\mathrm{mol\,l^{-1}}$ aqueous solution of potassium chloride. The two central compartments (R_1, L_1) were divided by a bipolar membrane ($A_m = 8\,\mathrm{cm^2}$), and 500 ml ion exchanged water was circulating independently.

The applied voltage was given by a direct current (d.c.) source (Kikusui, PAB18-1A). At this time the anion exchange layer of the bipolar membrane faced the anode and the cation exchange layer faced the cathode, and the distance between anode and cathode was 2.5 cm. During measurements, the applied voltage was kept constant at 15 V. The pH variation of each ion exchanged water was measured using pH meters (HM-20E, TOA). N_2 gas was circulated through each ion exchanged water to avoid acidification by CO_2 absorption for 2 h before and during the experiment. Further, the same experiments were carried out in the situation where the bipolar membrane was the other way round in order to evaluate any imperfection in the bipolar membrane.



AEM: Anion Exchange Membrane
CEM: Cation Exchange Membrane

Figure 1 Schematic diagram of the potential measurement when an intermediate region was installed

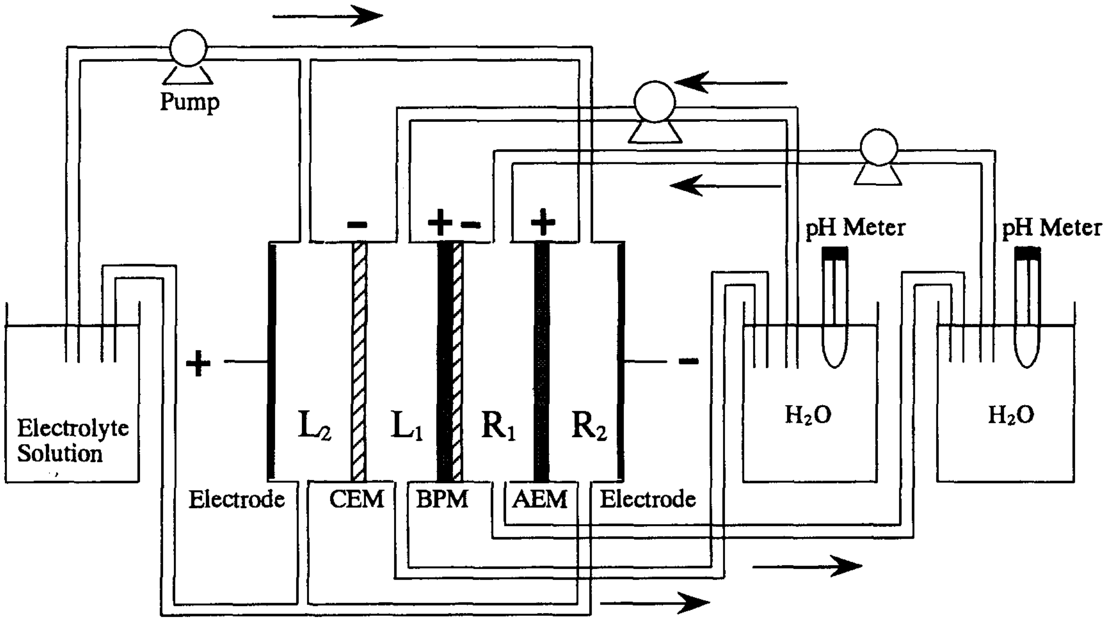
Rectification effect

The rectification effect across the membrane was measured with the feeler method (four-point method) as shown in *Figure 3*. The membrane was placed between two electrodialytic half-cells with $0.1\,\mathrm{mol\,dm^{-3}}$ aqueous solution of potassium chloride, and two Ag/AgCl electrode wires (diameter = 0.3 mm) on both surfaces of the membrane. The current was introduced through two Ag/AgCl electrode plates with areas $1\,\mathrm{cm^2}$. The applied voltage (V) was measured by a voltage meter (TOA, PM-16A) and current (I) by a picoammeter (TOA, AM-271A). The I–V curves were determined between measuring current and applied voltage across the membrane with the plates and wires 8 min after the measurement was started.

RESULTS AND DISCUSSION

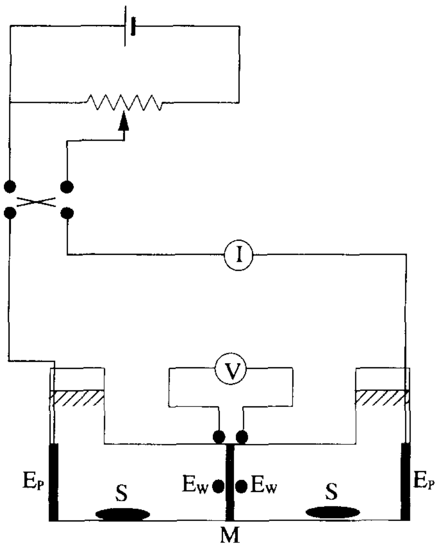
Membrane potential

The membrane potential of each bipolar membrane is shown as a function of electrolyte concentration in the external solution in *Figure 4*. Measurements were carried out at the same concentration of both compartments of the cell. The membrane potential remained constant



BPM: Bipolar Membrane
CEM: Cation Exchange Membrane
AEM: Anion Exchange Membrane

Figure 2 The test-scale cell of the production of acids and bases



M: Membrane
E_P : Ag/AgCl Plate Electrode
E_W: Ag/AgCl Wire Electrode
S : Stirrer

Figure 3 Schematic diagram of *I–V* measurement apparatus

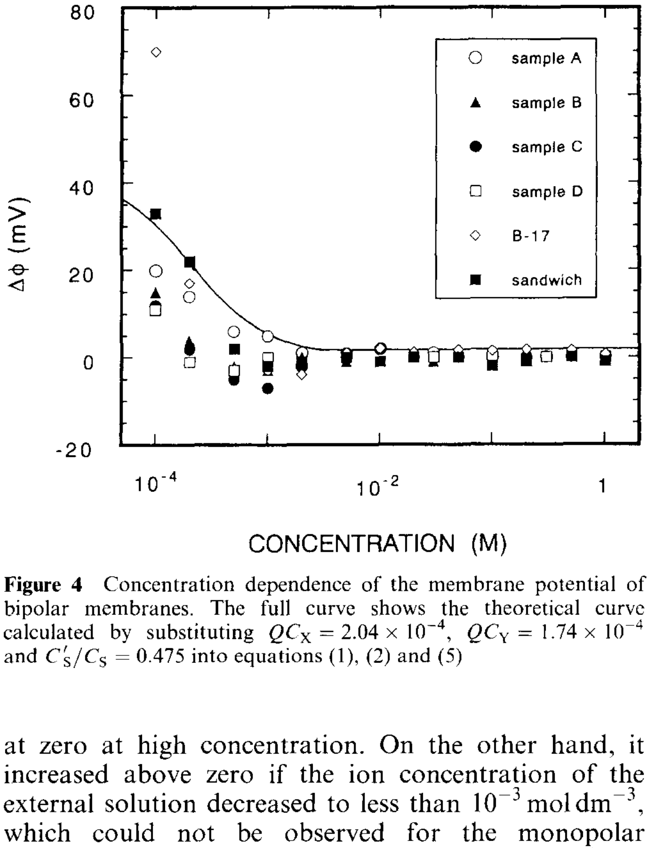


Figure 4 Concentration dependence of the membrane potential of bipolar membranes. The full curve shows the theoretical curve calculated by substituting $QC_X = 2.04 \times 10^{-4}$, $QC_Y = 1.74 \times 10^{-4}$ and $C'_S/C_S = 0.475$ into equations (1), (2) and (5)

at zero at high concentration. On the other hand, it increased above zero if the ion concentration of the external solution decreased to less than 10^{-3} mol dm^{-3}, which could not be observed for the monopolar membrane. At the lowest concentration of 10^{-4} mol dm^{-3} in this experiment, the membrane potential values of B-17, sandwich, sample A, sample B, sample C and sample D are positive and reduced in the order mentioned. In *Figure 1* if the concentration in the intermediate compartment, C'_S, is the same as that in the outside ones, C_S, no membrane potential can be observed. On the other hand, if C'_S is less than C_S a positive membrane potential is observed.

Taking *Figure 1* into consideration, application of Donnan equilibrium and the Nernst–Planck ion flux equation is one method to predict the membrane potential curve of the bipolar membrane in *Figure 4*[4,20,21]. It is expected that the flow is in a steady state where the electric current is zero across the membrane. We assume an intermediate region between the anion and the cation exchange layer in the membrane, and then the ion concentration of this region is different from that of external regions. Therefore potential differences are produced between the external solution and the intermediate region at both anion and cation exchange layers. The membrane potential of a cation ($\Delta\phi_1$) and an anion exchange layer ($\Delta\phi_2$) can be represented as the sum of two surface potentials and the diffusion potential in the membrane, respectively, which were given by Teorell, Meyer and Sievers (TMS) theory[20–22]:

$$\Delta\phi_1 = -\frac{RT}{F}\ln\left(\frac{C'_S\,[1+(2C_S/QC_X)^2]^{1/2}+1}{C_S\,[1+(2C'_S/QC_X)^2]^{1/2}+1}\right) - \frac{RT}{F}W\ln\left(\frac{[1+(2C'_S/QC_X)^2]^{1/2}+W}{[1+(2C_S/QC_X)^2]^{1/2}+W}\right) \quad (1)$$

$$\Delta\phi_2 = \frac{RT}{F}\ln\left(\frac{C'_S\,[1+(2C_S/QC_Y)^2]^{1/2}+1}{C_S\,[1+(2C'_S/QC_Y)^2]^{1/2}+1}\right) - \frac{RT}{F}W\ln\left(\frac{[1+(2C'_S/QC_Y)^2]^{1/2}-W}{[1+(2C_S/QC_Y)^2]^{1/2}-W}\right) \quad (2)$$

Here

$$(\omega_+ - \omega_-)/(\omega_+ + \omega_-) \equiv W \quad (3)$$

$$\gamma_+\gamma_-/k_+k_- \equiv Q^2 \quad (4)$$

C_X (mol dm^{-3}) and C_Y (mol dm^{-3}) are the fixed charge densities of the cation and anion exchange layers, respectively, defined as the fixed charge concentration per amount of water volume in the membrane; QC_X (mol dm^{-3}) and QC_Y (mol dm^{-3}) are the effective charge densities; ω (mol cm^2 J^{-1} s^{-1}) is the molar ion mobility, where mobility ratio ω_-/ω_+ is equal to that in water (=1.04); γ_+ and γ_- are the activity coefficients of cation and anion, respectively; k_+ and k_- are the partition coefficients of cation and anion, respectively; C_S (mol dm^{-3}) is the salt concentration of the external region and C'_S (mol dm^{-3}) is that of the intermediate boundary surface region. Though Q is a dimensionless parameter containing the activity and partition coefficients as shown in equation (4)[23,24], it is sometimes considered as an arbitrary parameter to fit experimental results to theoretical calculations without concern for the physical meaning of the activity and partition coefficients. QC_X and QC_Y can be estimated by the membrane potential method, and C_X and C_Y by the titration method. Q is supposed to be 0.1 to 0.2 for a normal ion exchange membrane from several experimental results[24].

The total membrane potential in a bipolar membrane, $\Delta\phi$ (V), is given as follows:

$$\Delta\phi = \Delta\phi_1 - \Delta\phi_2 \quad (5)$$

where both $\Delta\phi_1$ and $\Delta\phi_2$ are based on the external solution. In *Figure 4* the predicted result, which was calculated from equations (1), (2) and (5), is shown as the full curve in the case where $QC_X = 2.04 \times 10^{-4}$, $QC_Y = 1.74 \times 10^{-4}$ and $C'_S/C_S = 0.475$. The experimental results for the sandwich type membrane agree well with the predicted curve if the effective fixed charge densities in bipolar membranes are assumed to be about 0.0001 times smaller than those estimated from each layer separately: cation and anion exchange layers were prepared, the membrane potential of each monopolar layer was measured, and subsequently the experimental results were fitted to TMS theory to obtain the charge densities. Similar results are obtained for other membranes.

The effective fixed charge densities of bipolar membranes obtained by the method cited above are shown in *Table 1*. However, the fixed charge density of B-17 was measured by the titration method, because it was impossible to obtain separate anion and cation exchange layers in order to measure membrane potentials individually. Thus fixed charge densities C_X and C_Y of both layers in B-17 were evaluated as $20\,\mathrm{mol\,dm^{-3}}$ for the cation exchange layer and $4.7\,\mathrm{mol\,dm^{-3}}$ for the anion exchange layer, respectively. The effective charge densities QC_X and QC_Y, where Q is 0.1 to 0.2 as shown in the explanation of equations (1) and (2), were calculated as 2 to 4 and 0.47 to 0.94, respectively. For the cation exchange layer its value is comparatively high. As cited above it was defined as the fixed charge concentration per water volume in the membrane. The membrane structure of B-17 is supposed to be similar to Nafion, which implies that fixed charge groups are concentrated in small pores as cited above[19,25]. Since water can be stored in only these pores because of the hydrophobicity of polymer main chains, the charge density is estimated to be relatively high. For the anion exchange layer the effective charge density is similar to that of the other sample. Since it is composed not only of quaternary amine but also of secondary amine, the charge density is estimated to be lower than that of the cation exchange layer.

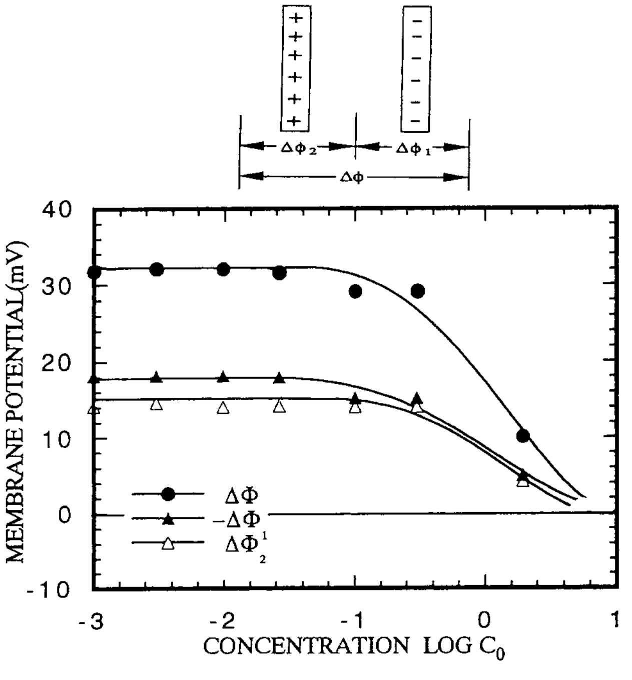


Figure 5 Concentration dependence of the membrane potential when an intermediate region was installed

Figure 5 shows a different experimental result of membrane potentials from *Figure 4*. An internal compartment was installed on this measurement, as shown in *Figure 1*, and the salt concentration ratio of the internal to the external compartment was kept constant ($C'_S/C_S = 0.5$). The result shows that a potential drop is observed at a salt concentration of about $1\,\mathrm{mol\,dm^{-3}}$. The point where the potential drops is shifted to the high-concentration side if it is compared with *Figure 4*. The effective fixed charge densities obtained by curve fitting with equation (5) in this experiment are the same as the original charge densities of monopolar membranes, which are shown in *Table 1*. The large drop of the effective charge density QC_X or QC_Y is attributed to the decrease of Q, since the fixed charge density C_X or C_Y should not be altered. Q is a function of the activity and partition coefficients of the cation and anion as shown in equation (4). If the activity coefficient of the ions is lowered in the membrane, the Q value is reduced. Decrease of activity coefficient in the membrane has already been pointed out by Lakshminarayanaiah[26]. However, if it is exerted through the whole membrane, it contradicts the results of the rectification effect and water splitting observed, because they cannot be observed under a low charge density. Therefore, this contradiction may be solved based on either of the following two proposals: (1) It may be suggested that the apparent decrease of charge density takes place only at surfaces facing the intermediate region, which is due to mutual interaction of charge groups between the anion and cation exchange layers. (2) The salt concentration in the intermediate region prefers to take a smaller value than that of external solution in the lower-concentration region less than $10^{-3}\,\mathrm{mol\,dm^{-3}}$. We had better consider that the large shift of membrane potential is caused by a Donnan potential rather than a diffusion potential, because the difference of ion mobility between cation and anion is very small in the case of KCl. These problems might be discussed in the forthcoming consideration.

pH change under constant applied voltage

A bipolar membrane can separate water into hydrogen and hydroxyl ions that diffuse to cathode and anode, respectively, which is called water splitting[8–11]. The schematic drawing of acid and base purification is illustrated in *Figure 6*. If a direct voltage of 15 V is applied in the proper direction, which is from the cation exchange to the anion exchange layer, H_2O diffusing into the intermediate boundary region is dissociated into H^+

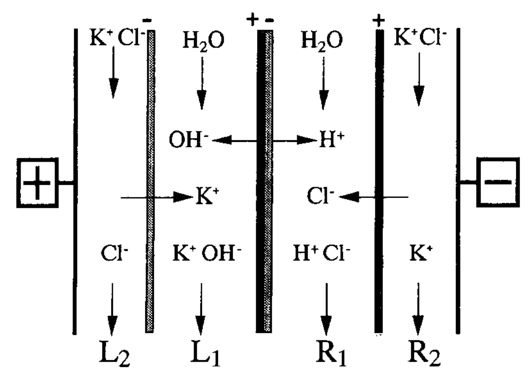


Figure 6 Water splitting process

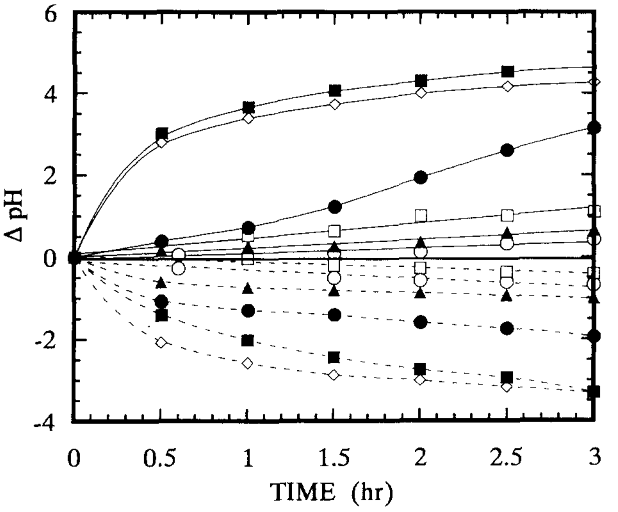


Figure 7 Time dependences of pH change: (○) sample A; (▲) sample B; (●) sample C; (□) sample D; (◇) B-17; (■) sandwich. Full and broken curves show pH changes at anode (R_1) and cathode side (L_1)

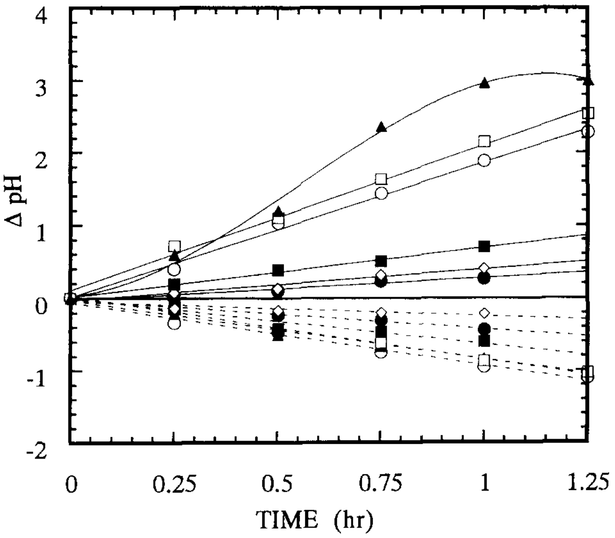


Figure 8 Time dependences of pH change when the membrane was set reversely, i.e. where the anion exchange layer faced the cathode: (○) sample A; (▲) sample B; (●) sample C; (□) sample D; (◇) B-17; (■) sandwich. Full and broken curves show pH changes at anode (R_1) and cathode side (L_1)

and OH^- ions under the electric field. Electroneutrality is satisfied for the reason that K^+ and Cl^- ions permeate through monopolar cation and monopolar anion exchange membranes from the side compartments (R_2, L_2) to the two central compartments (R_1, L_1), respectively, where ion exchanged water is circulating independently. Thus acid in R_1 and base in L_1 are produced, respectively. The experimental result is shown in *Figure 7*. The total currents across sample A, sample B, sample C, sample D, B-17 and sandwich membranes are 0.0036, 0.0045, 0.045, 0.007, 0.11 and 0.15 mA cm^{-2}, respectively. Large pH changes are observed in B-17, sandwich type and sample C whose thickness of anion exchange layer is equal to half that of the cation exchange layer. Acid and base production may proceed satisfactorily in those three samples cited above. It is also observed that the pH change in R_1 is larger than that in R_2 for each sample. If a part of H^+ and/or OH^- flows in the wrong direction owing to imperfection of the membrane, which is called leakage, such a phenomenon can be explained according to the amount of the difference of leaked H^+ and OH^-. It is considered that the amount of H^+ leaked from R_1 to R_2 through the anion exchange membrane is larger than that of OH^- leaked from L_1 to L_2 through the cation exchange membrane.

Experimental results for the situation where the bipolar membrane is installed the other way round between the cells are shown in *Figure 8*. If the membrane structure is ideally perfect, dissociated ions of H^+ and OH^- cannot penetrate to the central compartments (R_1, L_1) because of the reversely installed bipolar membrane and no pH change is observed. However, if it is imperfect because of defect formation, H^+ and OH^- ions leak to R_1 or L_1 and a pH change is observed[27]. The large shift of pH in *Figure 8* shows that a large amount of leaked H^+ and OH^- ions is observed. Thus we can conclude that the pH change under constant applied voltage in reversely installed bipolar membranes depends on the leakage of ions.

Water splitting includes two different phenomena: water dissociation into hydrogen and hydroxide ions, and ion diffusion through a charged layer. In order to discuss the water splitting effect, it is necessary to consider these phenomena separately in spite of its difficulty. Let us now focus on only hydrocarbon type membranes. There are great differences of pH change at constant applied voltage in each sample. This result may be due to: (i) defects such as pores formed during membrane formation; and (ii) the state of the intermediate region between the cation and the anion exchange layer.

Drying at 125°C causes pore formation easily. For samples A and D, where the anion exchange layers are thicker than those of the other samples, the anion exchange layers of those samples were prepared by casting several times to protect the phase separation. The process of heating and cooling is repeated several times and this may cause pores to form more easily. Pores reduce the ion separability in each ion exchange layer because it cannot protect the diffusion of co-ion.

The state of the intermediate region, where positive and negative charged groups are mixed, also influences the water splitting effect. A mixture of different charged groups causes a gradual potential change between two layers. It reminds us of reduction of water dissociation ability. On the other hand, such an effect for the sandwich type membrane, which is composed of only quaternary amine and sulfonic acid as a fixed charge groups and has no polymer mixture in the intermediate region but still realizes a sharp potential drop across it, is superior to almost all of the other samples as shown in *Figure 7*. This fact seems to support the assumption that the water molecule dissociates into cation and anion obeying the second Wien effect[12–14]. However, the pH change in B-17, which is composed of a mixture of secondary and quaternary amines as fixed charge groups in the anion exchange layer, is almost the same as that in the sandwich type membrane though it has an intermediate region where charged groups are changing their signs gradually from negative to positive. This shows that water dissociation takes place also by chemical reaction on secondary amines. This is one piece of

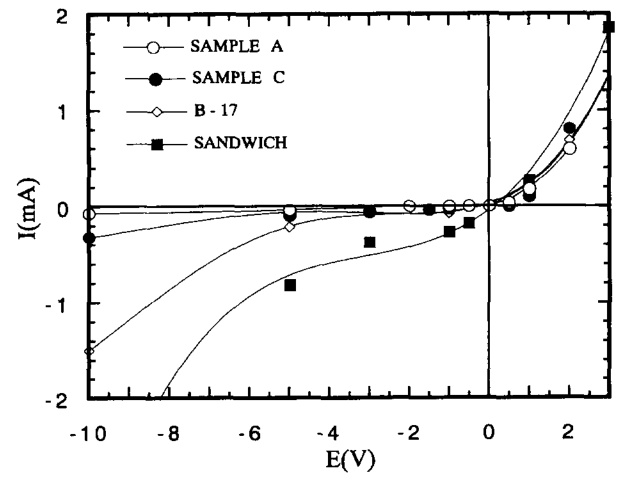


Figure 9 Current–voltage curves of membranes

evidence that Simons has suggested that the chemical reaction takes place at the membrane interface on the anion exchange side[15–17]. At this moment it is considered that both the second Wien effect and chemical reaction on amine groups are effective for water dissociation in the membrane.

Rectification effect

The current–voltage curves for samples A, C, B-17 and sandwich type are shown in *Figure 9*. The results of samples B and D are similar to sample A. The rectification effect was observed in all samples. So the theories concerned with semiconductor p–n junctions[1–3,11] are applied to the behaviour of ions in a bipolar membrane. The counter-ions of the anion and cation exchange layers are applied to electron and hole, respectively. When the applied voltage is less than −3 V, the electric current, which flows during the time of applying the reverse bias, is due to H^+ and OH^- ions produced by water splitting. For samples C, B-17 and sandwich type membrane, this current is observed. As all of them were proved to have high efficiencies at water splitting, this result was consistent with the previous one. In the case of the sandwich-type membrane, a relatively high current compared with samples C and B-17 was observed in spite of the application of a low reverse bias. This is due to ions except H^+ and OH^- (ref. 14) that are already dissolved in the space between the anion and cation exchange membranes from the ion exchange membranes. Though a sandwich-type membrane shows a large pH change during water splitting measurement, it is not suited for practical use because of the space formation due to the separation of the intermediate region. Samples A, B, C and D are prepared using the same materials and method though their thicknesses are different from each other. It is supposed that the intermediate state is the same. Resistance in the forward direction is very high for samples A, B and D, and reduced for sample C as shown in *Figure 9*. On the other hand, the pH change of sample C is much larger than that of samples A, B and D as seen in *Figure 7*. It shows that the water splitting effect of sample C is superior to the other samples. The high resistance and low pH change for samples A, B and D remind us of the formation of a deionized water layer in the intermediate region if their component material and preparation method cited above are different from those of sample C. However, we need further structural investigation to give a final decision.

In closing, the relationship between membrane potential and the water splitting ability of membranes was discussed. The membrane potential of B-17 was higher than that of sample A on the low-concentration side. The membrane potential in low-concentration limits is:

$$\Delta\phi(C_S \to 0) = -\frac{2RT}{F}\ln r \qquad (6)$$

where

$$r = C'_S/C_S$$

Therefore the ratio C'_S/C_S influences the membrane potential. The membrane potential for the sample with low pH change was lower than that of high pH change at low concentration, since the ratio C'_S/C_S of the former was reduced compared with the latter. One of those reasons is the defects formed during casting. Those defects cause leakage of ions in the intermediate region to decrease the concentration difference between C'_S and C_S.

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