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Concentration Polarization Phenomena in Ion-exchange Membrane Electrodialysis. I. Studies of the Diffusion Boundary Layer by Means of Six Different Measurements[*1]

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The behavior of the diffusion boundary layer in the electrodialysis using ion-exchange membranes, mainly a cation-exchange membrane, was studied by means of six different measurements: 1) the determination of the current-voltage curve or the current-(voltage/current) curve; 2) the relation of the pH change of the solution to the current density; 3) the relation of the charge retention, *i. e.*, the sum of the diffusion potential and the membrane potential generated from the concentration gradient across the membrane immediately after the current is shut off, to the current density; 4) the time required to reach a constant current value, namely, to obtain a stationary diffusion boundary layer, when a constant voltage is supplied to the system, *versus* the current density; 5) the change in the transport number of the counterion in the membrane with the current density, and 6) the relation of the permselectivity between sodium ions and potassium ions to the current density. The interrelation among these results was also examined. The quantity of hydrogen ions or hydroxide ions passing through the membrane increases abruptly at a current density lower than that at which the concentration at the membrane-solution interface in the desalting side attains its minimum. It was newly observed that the results of all the measurements, except for the pH change of the solution, show abnormal phenomena at a current density about twice the limiting current density.

In the electrodialysis using ion-exchange membranes, one of the most important phenomena is the concentration polarization at the membrane-solution interfaces. The concentration gradient is observed on both sides of the membrane-solution interfaces; ions are accumulated or depleted at the interfaces as a result of the difference in the transport numbers in the solution and in the membrane. This phenomenon, called the concentration polarization, is especially important at the membrane-solution interface on the desalting side.

Peers,[1] Rosenberg *et al.*,[2] Frilette,[3] and other investigators studied this phenomenon by observing the current-voltage curve of the membrane-solution system. Uchino *et al.*[4] and Gregor *et al.*[5] observed limiting current density through the relation of the current efficiency to the current density. Cooke[7-9] and Onoue[10] evaluated the interfacial concentration at the membrane-solution interface on the desalting side by determining the charge retention. Though the concentration polarization phenomenon has been studied in the various ways mentioned above, however, there still remain some uncertainties, and the interrelation among the results obtained by means of various measurements is not clear.

In this investigation this phenomenon was observed by means of the following six measurements, with an emphasis on the observation of the current-voltage curve of the membrane-solution system, and the results were compared with each other. The six measurements are: 1) the determina-the pH change of the solution in the electrodialysis system, while Kressman and Tye[6] observed the

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1) A. M. Peers, *Discussions Faraday Soc.*, **21**, 124 (1956).

2) N. W. Rosenberg, J. A. Kirkham, C. E. Tirrell and N. E. Saliba, *Saline Water Research and Development Progress Report,* No. 1 (U.S. Dept. of Interior), April,

3) V. J. Frilette, *J. Phys. Chem.*, **61**, 168 (1957).

4) T. Uchino, S. Nakaoka, H. Hani and T. Yawataya, *Denki Kagaku* (*J. Electrochem. Soc. Japan*), **26**, 366 (1958).

5) H. P. Gregor and M. A. Peterson, *J. Phys. Chem.*, **63**, 2201 (1964).

6) T. R. E. Kressman and F. L. Tye, *Discussions Faraday Soc.*, **21**, 185 (1956).

7) B. A. Cooke, *Electorchim. Acta*, **3**, 307 (1961).

8) B. A. Cooke, *ibid.*, **4**, 179 (1961).

9) B. A. Cooke, *ibid.*, **5**, 216 (1961).

10) Y. Onoue, *Denki Kagaku* (*J. Electrochem. Soc. Japan*), **30**, 415 (1962).

tion of the current-voltage curve or the current-(voltage/current) curve; 2) the relation of the pH change of the solution to the current density; 3) the relation of the charge retention, *i. e.*, the sum of the diffusion potential and the membrane potential generated from the concentration gradient across the membrane immediately after the current is shut off, to the current density; 4) the time required to reach a constant current value, namely, to obtain a stationary diffusion boundary layer, when a constant voltage is given to the system, *versus* the current density; 5) the change in the transport number of the counterion in the membrane with the current density, and 6) the permselectivity (relative transport number) of potassium ions to sodium ions *versus* the current density.

Experimental

Ion-exchange Membranes. Throughout this investigation, commercial ion-exchange membranes prepared by the "Paste Method," *i. e.*, a cation-exchange membrane, NEOSEPTA CL-2.5T, and an anion-exchange membrane, NEOSEPTA AVS-4T, were used. The characteristics of these membranes are shown in Table 1.

TEBLE 1. CHARACTERISTICS OF ION EXCHANGE MEMBRANES

Name	NEOSEPTA CL-2.5T	NEOSEPTA AVS-4T*1
Type	Strongly acidic cation exchange	Strongly basic anion exchange
Backing	Polyvinyl chloride	Polyvinyl chloride
Thickness (mm)	0.15—0.17	0.15—0.17
Burst strength (kg/cm^2)	3—4	4—6
Electric resist.*2 (Ω-cm^2)	2.7—3.2	3.7—4.7
Transport number*3	>0.98	>0.98
Water content*4	0.30—0.40	0.25—0.35
Ion exchange cap.*5	1.8—2.0	1.5—2.0

*1 Univalent anion permselective.

*2 Equilibrated with 0.5 N NaCl soln. at 25.0°C.

*3 Measured by electrodialysis with 0.5 N NaCl soln., current density: 10 mA/cm^2, at 25.0°C.

*4 Equilibrated with 0.5 N NaCl soln., [g H_2O/g Na-form dry memb. (or Cl-form)].

*5 [meq./g Na-form dry memb. (or Cl-form)].

Measurements. 1) *Current-voltage Curve.* The current-voltage curve was observed by using the apparatus shown in Fig. 1, which was also used in the other five measurements. In Fig. 1, 1 and 4 are silver chloride plate electrodes, and 2 and 3 are silver chloride wire probe electrodes which are put close to the membrane (about 2 mm apart). The current was increased automatically by means of a slow moving motor connected with a regulated direct current supply, Metronix Corp. Model 535. As the current-voltage curve varies with an increase in the speed of the current when it is too large, the increase in the speed was adjusted so as not to affect the current-voltage curve. The values of the current and the voltage were recorded on an X-Y recorder, Watanabe Instruments Corp. Type WX-406.

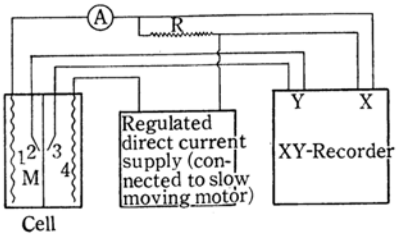


Fig. 1. Equipment used in measurement of current-voltage curve.
R: standard resistance
A: amperemeter
M: membrane
1, 4: silver chloride plate electrodes
2, 3: silver chloride wire probe electrodes

2) *pH Change in the Solution.* A cell has a cation- or an anion-exchange membrane (4.0 cm^2 in area) to be examined and shielding cation- and anion-exchange membranes (36 cm^2 in area). An aqueous 0.500 N sodium chloride solution (3.0*l* in volume) was circulated in the desalting compartment (10 mm thick) at a laminar flow of 4.2 cm sec^{-1}, and an aqueous 2.500 N sodium chloride solution (50 m*l* in volume) was circulated in the concentrating compartment (3 mm thick) at a laminar flow of 1.3 cm sec^{-1}. The pH change in the solution in the concentrating compartment was observed continuously for an hour by using a glass electrode pH-meter, Denki Kagaku Keiki Co. Model MG-1, connected to an X-t recorder, Toa Electronics. EPR-2T, while the current was broken by the dripping of the solution. The difference in the pH of the solution between the starting time and after an hour was evaluated at various current densities at 30.0°C.

3) *Charge Retention.* In preparing Fig. 1 the X-t recorder was used instead of the X-Y recorder, and two turn-over switches were added between the 1 and 4 electrodes and the direct current supply, and between the 2 and 3 electrodes and the X-axis of the X-t recorder. After the membrane-solution system had been electrodialized at a constant current density until a stationary diffusion boundary layer had been obtained, the current was shut off and the charge retention was picked up with the 2 and 3 electrodes. The scanning speed of a pen on the recorder is more than 300 mm/sec, faster than that of turning switches. The decrement curve of the charge retention at various current densities was recorded on the X-t recorder. These measurements were carried out with a natural convection of an aqueous 0.104 N sodium chloride solution by using a membrane 2.0 cm^2 in area and at 25.0°C.

4) *Transport Number.* The cell was separated into two compartments by a membrane with an area of 2.0 cm^2. After the electrodialysis had been carried out at a constant current density for an hour using an aqueous 0.104 N sodium chloride solution, the transport number was calculated from the change in the concentration of chloride ions in each compartment and the amount of the electricity was measured with a copper coulometer. These measurements were carried

out with a natural convection and at various current densities at 25.0°C.

5) *Time Required to Obtain a Stationary Diffusion Boundary Layer*. When a constant voltage was supplied to the cell, the current passing through the membrane, as recorded on the X-t recorder, gradually decreased because of the growth of the diffusion boundary layer, the stationary current was then obtained. The time required to reach the constant current value was measured at various constant voltages. The measurements were made with a natural convection of an aqueous 0.104 N sodium chloride solution by using a membrane with an area of 2.0 cm² and at 25.0°C.

6) *Permselectivity*. The cell was separated into two compartments by a membrane with an area of 4.0 cm². After the system had been electrodialized at a constant current density for an hour using a mixed solution of 0.053 N sodium chloride and 0.053 N potassium chloride, the permselectivity of potassium ions to sodium ions was calculated from the change in the concentration in each compartment. The chloride ions were analysed by the Mohr method, while the potassium ions were analyzed by the gravimetric method using tetraphenylborate. The measurements were made with a natural convection and at various current densities at 25.0°C. The permselectivity is defined as $(t_K^M/t_{Na}^M)/(C_K/C_{Na})$. t_K^M and t_{Na}^M are respectively the transport numbers of the potassium ions and the sodium ions in the membrane, and C_K and C_{Na} are the concentrations of potassium ions and sodium ions respectively in the bulk solution.

Results and Discussion

Typical examples of the current-voltage curve and of the current-(voltage/current) curve obtained with a cation-exchange membrane, NEOSEPTA CL-2.5T, in an aqueous sodium chloride solution are shown in Fig. 2. A similar curve was obtained with an anion-exchange membrane, NEOSEPTA AVS-4T, in an aqueous sodium chloride solution. In this curve the voltage and the (voltage/current) of the system are anomalous at three different current densities, *i. e.*, A-, B-, and C-points. The current density at the A-point has been defined as the limiting current density.[11] The (voltage/current) ratio shows its maximum value at the B-point, a gradual decrease between the B- and C-points, and an abnormal decrease at the C-point.

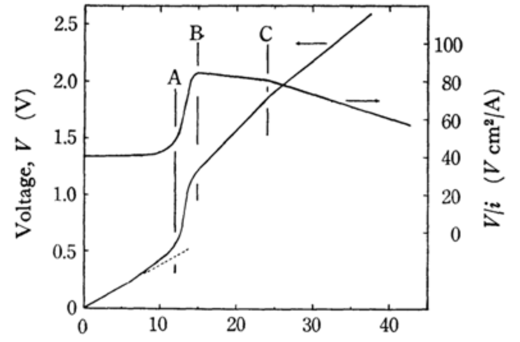
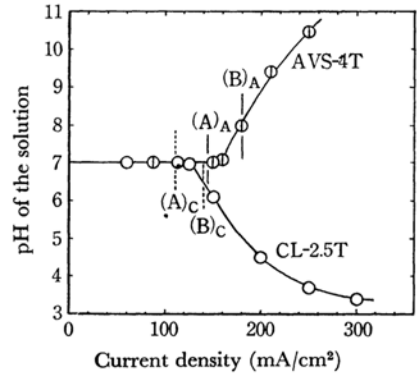


Fig. 2. An example of current-voltage curve and current-V/i curve.
Membrane: CL-2.5T (2.0 cm² in area)
Solution: 0.104 N NaCl aqueous solution in natural convection at 25.0°C

The relationship between the pH change of the solution and the current density is shown in Fig. 3, in which the A- and B-points as determined from current-voltage curves are added. The pH change in the solution was detected between the A- and the B-points.



Fi. 3. Relation between pH of the solution in the concentrating side of membrane after current was passed for an hour and current density.
0.500 N NaCl aqueous solution let to flow in the desalting side at 4.2 cm sec⁻¹, and 2.500 N NaCl aqueous solution in the concentrating side at 1.3 cm sec⁻¹.
$(A)_C$, $(B)_C$: A-, B-point in CL-2.5T
$(A)_A$, $(B)_A$: A-, B-point in AVS-4T

The experimental results on the charge retention are shown in Fig. 4. The charge retention is

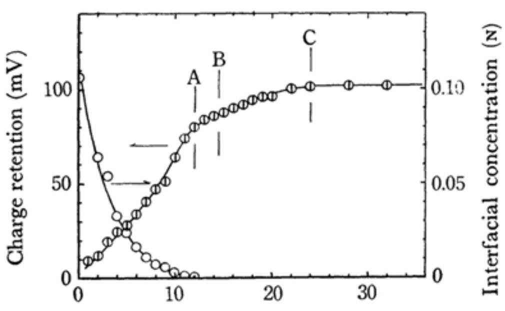


Fig. 4. Relation of charge retention and interfacial concentration in desalting side of membrane evaluated from charge retention to current density.
Membrane: CL-2.5T
Solution: 0.104 N NaCl aqueous solution in natural convection

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[11] D. A. Cowan and J. H. Brown, *Ind. Eng. Chem.*, **51**, 1445 (1959).

the sum of the diffusion potential and the membrane potential. For example, when the electrodialysis is carried out by using the cation-exchange membrane in an aqueous sodium chloride solution, the charge retention is shown by the following equation[7,10)]:

$$E=\frac{\boldsymbol{RT}}{\boldsymbol{F}}2(\bar{t}_+-t_+)\ln\frac{(C_0+\Delta C)\gamma_1}{(C_0-\Delta C)\gamma_2} \tag{1}$$

$\boldsymbol{t}_+$ and t_+ are transport numbers of the counterion in the cation-exchange membrane and in the solution, C_0 is the concentration in the bulk solution, ΔC is the difference in the concentration between the membrane-solution interfaces and the bulk solution, and γ_1 and γ_2 are activity coefficients of the counterion at the membrane-solution interfaces on the concentrating side and on the desalting side respectively. The charge retention increases abruptly at current densities lower than the A-point, and increases slowly between the A- and C-points. No change was observed at the B-point, and a constant value was obtained at current densities higher than the C-point. The same results were obtained with the anion-exchange membrane. The concentration at the membrane-solution interface on the desalting side could be calculated from Eq. (1) as long as the quantity of hydrogen ions is negligible in comparison with the quantity of sodium ions in the diffusion boundary layer and in the bulk solution. The calculated values are shown in Fig. 4.

The relation of the transport number to the current density is shown in Fig. 5. The transport number shows its maximum value near the A-point; it gradually decreases between the B- and C-points and suddenly above the C-point.

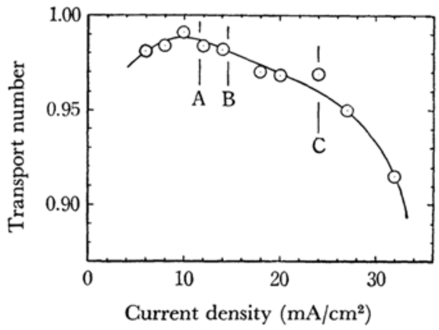

Fig. 5. Relation of transport number to current density.
Membrane: CL-2.5T
Solution: 0.104 N NaCl aqueous solution in natural convection

The relation between the time required to obtain a stationary diffusion boundary layer and the current density is shown in Fig. 6. The change in the current with time is shown in Fig. 7 as an example. The time is defined as the time interval between a and b in Fig. 7. No change was observed at the A-point, the maximum was obtained near the B-point, and the duration decreased abruptly at current densities higher than the C-point. The stationary diffusion boundary layer was achieved on balancing the flux of ions passing through the membrane with that of ions transporting to the membrane-solution interface on the desalting side. When the current density increases, the concentration at the membrane-solution interface on the desalting side decreases and the time increases. When the interfacial concentration on the desalting side attained its minimum, the time reached its maximum. Thus, the maximum duration is obtained in the vicinity of the B-point. The duration decreases at current densities higher than the B-point. This behavior is analogous to the relation of the transition time to the current density in the chronopotentiometry. The transition time is

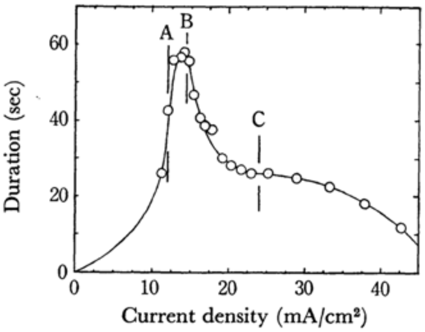

Fig. 6. Relation of duration required to obtain stationary diffusion boundary layer to current density.
Membrane: CL-2.5T
Solution: 0.104N NaCl aqueous solution in natural convection

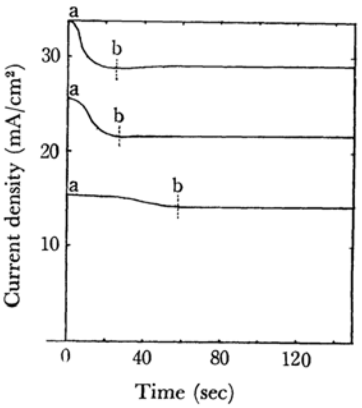

Fig. 7. Decrement curves of current when constant voltage is given to cation exchange membrane-solution system.
Time between a and b is the duration required to obtain the stationary diffusion boundary layer.

shown as follows:[12)]

$$\tau^{1/2}=\frac{nF\pi^{1/2}D^{1/2}C}{2i} \tag{2}$$

C is the concentration of the solution; i is the current density; τ is the transition time; D is the diffusion coefficient, and n and F are the valency and the Faraday constant respectively. The $\tau\propto 1/i^2$ relation is inferred at the current densities between the B- and C-points in Fig. 6. However, the decrease in the duration at current densities higher than the C-point is anomalous.

Figure 8 shows the permselectivity of potassium ions to sodium ions at several different current densities. As the permselectivity of potassium ions to sodium ions is larger than unity, the concentration of sodium ions becomes larger than that of potassium ions at the membrane-solution interface on the desalting side when the current increases, and so the permselectivity, p^{K}_{Na}, decreases. In Fig. 8 no change is observed at the A- and B-points, but some change is observed at current densities higher than the C-point.

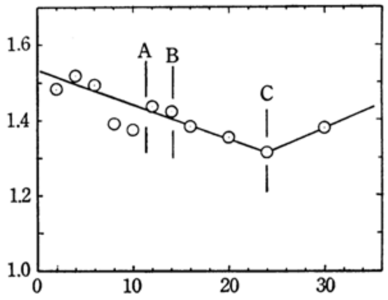

Fig. 8. Reltation of permselectivity between sodium ion and potassium to current density.
Membrane: CL-2.5T
Solution: Mixed solution of 0.053 N KCl and 0.053 N NaCl in natural covection
P^{K}_{Na}: Permselectivity between K^+ and Na^+.

The relation among the six experimental results mentioned above will now be discussed with emphasis on the interpretation of the A-, B-, and C-points. Near the A-point, the voltage of the membrane-solution system suddenly begins to increase, the increase in the charge retention becomes slower, the period required to obtain a stationary diffusion boundary layer increases continuously, and the transport number of the counterion in the membrane attains its maximum. The results on the current-voltage curve, the charge retention, and the duration show a further decrease in the concentration at the membrane-solution interface on the desalting side near the A-point. It was reported in a previous paper[6)] that the transport number of sodium ions in the cation-exchange membrane decreases at higher current densities after showing its maximum value as a result of the increase in the transport number of hydrogen ions in the membrane. However, the pH change in the solution was detected between the A- and B-points. The pH change in the solution might arise from the following three causes. First, the pH change in the solution may be on account of the increase in the rate of the dissociation of water under a strong electric field; however, this has scarcely any effect on the pH change in the solution because the electric field of 10^4 V/cm increases the dissociation constant by only 1 percent.[13,14)] Secondly, the ion-exchange membranes used in this experiment are reinforced with polyvinyl chloride and so would have conjugated double bonds through the decomposition of polyvinyl chloride during the introduction of sulfonic acid groups and other treatments.[15)] If there were an electronic conduction based on conjugated double bonds, the ion-exchange membranes would function as electrodes. Therefore, the electrolysis of water could occur at the membrane-solution interfaces and cause the pH change in the solution. However, as the pH change in the solution was nearly constant in the ion-exchange membranes reinforced with other polymers, this effect would scarcely have any relation with the pH change in the solution. Thirdly, when the current density increases, the concentration of sodium or chloride ions on the desalting membrane-solution interface decreases and becomes nearly equal to the concentration of hydrogen or hydroxide ions (10^{-7} mol/l). Consequently, the quantity of hydrogen or hydroxide ions which pass through the membrane increases in comparison with that of sodium or chloride ions. Hydrogen or hydroxide ions pass through the membrane at current densities lower than the A-point, but the pH change in the solution could not be observed because it is too small to be detected by a usual pH-meter. It may be considered that the pH change in the solution in the electrodialysis is caused by the third reason. We attempted to observe the pH change in the solution visibly by adding a pH-indicator to the solution. However, the current-voltage curve observed in the solution with the pH-indicator differs from those in the solution without the pH-indicator and are not reproducible. The adsorption of the pH-indicator on the membrane would change the characteristics of the membrane.

The concentration of the desalting membrane-solution interface attains its minimum at the B-

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[12)] *Denki Kagaku Binran* (*Handbook of Electrochemistry*), 344 (1964).

[13)] H. P. Gregor and I. P. Miller, *J. Am. Chem. Soc.*, **86**, 5689 (1964).

[14)] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[15)] C. Forgacs and G. Stein, *J. Phys. Chem.*, **69**, 4221 (1965).

point. This is unquestionably established by the observation of the current-(voltage/current) curve and the duration time. The pH change in the solution, the charge retention, and the permselectivity, $P_{\mathrm{Na}}^{\mathrm{K}}$, do not show any change at the B-point. Figure 2 shows that the current-(voltage/current) curve decreases at current densities higher than the B-point. In order to make clear the reason for this decrease, the current-voltage curve and the current-(voltage/current) curve were observed using the cation-exchange membrane, NEOSEPTA CL-2.5T, in an aqueous hydrochloric acid solution. The results are shown in Fig. 9.

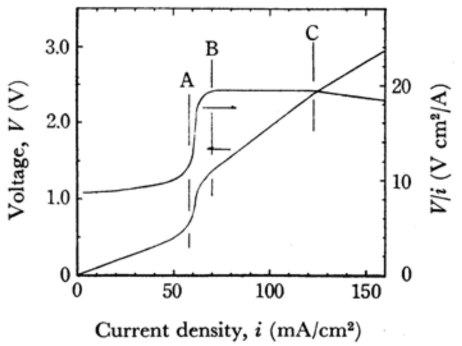

Fig. 9. Current-voltage and current-V/i curve measured in hydrochloric acid solution.
Membrane: CL-2.5T
Solution: 0.100 N HCl aqueous solution in natural convection at 25.0°C

The current-voltage curve does not decrease, but is parallel with the current-axis, between the B- and C-points, while it decreases above the C-point. Accordingly, the decrease in the current-(voltage/current) curve in a sodium chloride solution between the B- and C-points is due to the increase in the transport number of hydrogen ions in the membrane and their high conductivity. At and above the C-point, the current-(voltage/current) curve decreases still more, the duration time decreases abnormally, the decrease in the transport number is great, the permselectivity, $P_{\mathrm{Na}}^{\mathrm{K}}$, increases, and the charge retention attains a constant value. This behavior at and above the C-point can not yet be explained.

This paper has mainly described measurements of the cation-exchange membrane. The same results were obtained on the anion-exchange membrane, NEOSEPTA AVS-4T. It was reported in an earlier paper7) that the extent of the pH change in the solution of the anion-exchange membrane system is larger than that in the cation-exchange membrane system. However, there is no difference between the cation-exchange membrane system and the anion-exchange membrane system in this experiment using NEOSEPTA. Figure 3 shows that the pH of the solution shifts to about 3 in the cation-exchange membrane system and to about 10 in the anion-exchange membrane system at a high current density.

The A-, B-, and C-points measured by means of the six measuring methods are relative values. These points vary with various factors, such as the concentration, the temperature, and the flow velocity of the solution, the structure of the cell, the ionic species, and so on. The effect of these factors on the limiting current density has been studied and will be reported on subsequent papers.