LBL-16557
UC-94cd

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 19 1983

LIBRARY AND
DOCUMENTS SECTION

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

R.T. Ruggeri and T.R. Beck

July 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

APPLIED SCIENCE DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-16557 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-16557

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

FINAL REPORT

Prepared for:
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
Berkeley, California 94720

By: R. T. Ruggeri
T. R. Beck, Principal Investigator

ELECTROCHEMICAL TECHNOLOGY CORP.
3935 Leary Way N.W.
Seattle, Washington 98107
(206) 632-5965

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4511710.

July 1983

SUMMARY

This report summarizes the effort to extend the theory and measurement techniques of multicomponent mass transfer in membranes. The results of the early experiments suggested that the transport properties might be accurately determined using a radiotracer method, and that certain transport properties of Nafion might depend strongly on the applied current density. Therefore, a program was initiated to investigate the effects of current density on the membrane transport properties using a radiotracer technique similar to that described by Meares and Sutton (1). The solubilities of sodium and chloride ions in Nafion 7-1100 have also been determined. The main body of this report describes the radiotracer experiments. The ion solubility results have been reported previously (2-5) and are included in Appendix B.

The effect of current density on the sodium ion transference number is slight, as shown in Fig. 1. The radiotracer results have been compared to the results obtained by more conventional means using the Hittorf method with concentrations determined by specific-ion titration. Table 1 lists the Hittorf results. Approximate standard deviations are also listed in Table 1 and are shown as error bars in Fig. 1. Figure 2 shows how the transport number of water changes with current density.

It is concluded that the radiotracer method is a viable means of determining multiple transport numbers and self-permeability coefficients in a single experiment. Further, the method is at least as accurate as the more conventional Hittorf method. It is apparent that these radiotracer methods can be effectively utilized in the investigation of multicomponent mass transfer in a wide variety of membranes.

---

(1) P. Meares and A. H. Sutton, J. Colloid Interface Sci., 28, 118 (1968).

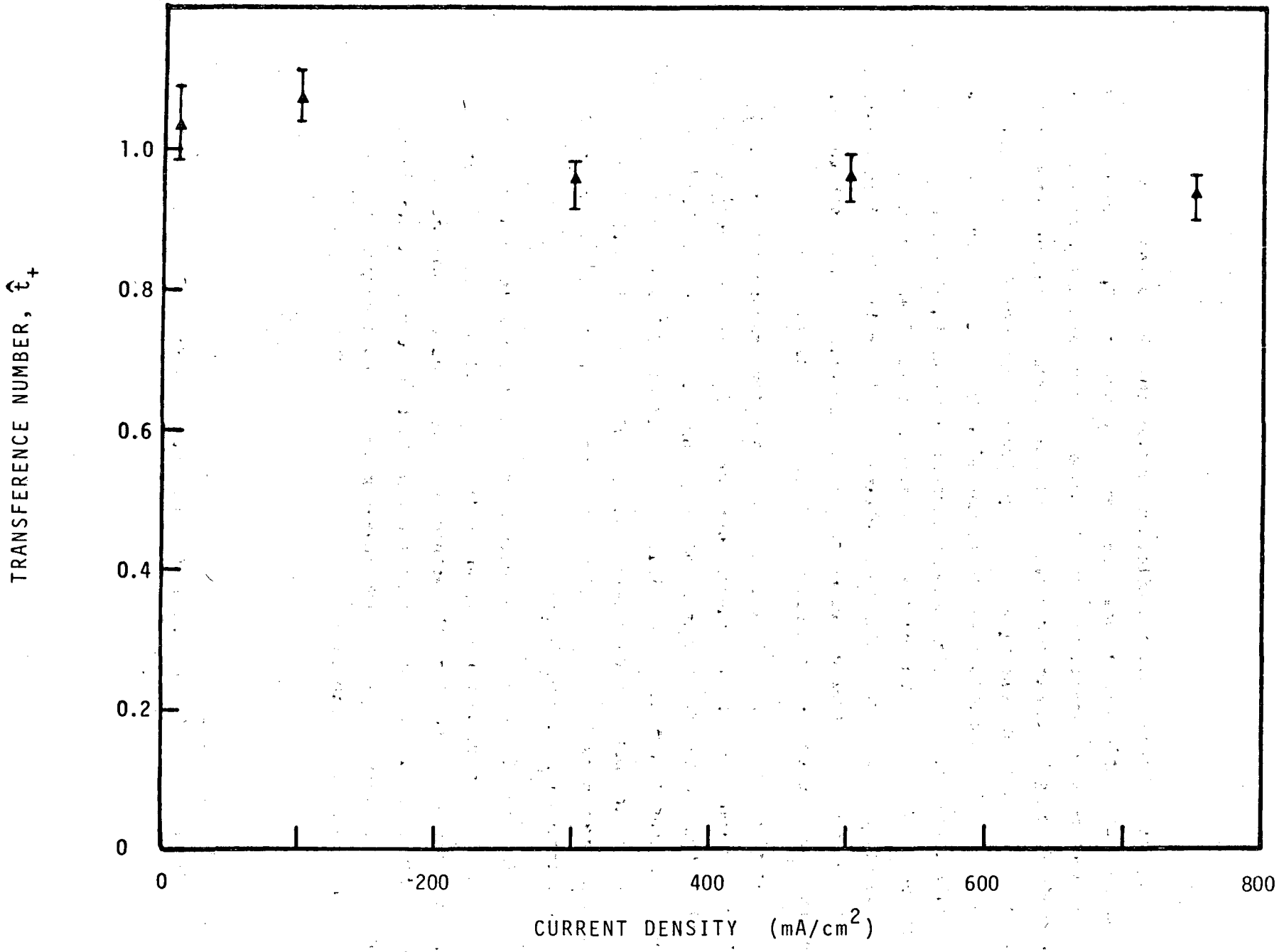

Fig. 1. Sodium-ion transference numbers obtained by radiotracer experiments. Nafion membrane in 0.1 N NaCl solution, at 27°C.

Table 1

Hittorf Results

i (mA/cm^2)	Charge Passed (C)	Concentration Change (M)	$\hat{t}_+$	$\hat{t}_+$ Standard Error
10	9.54	0.0184	1.196	0.17
100	15.75	0.0228	0.898	0.12
300	17.55	0.0267	0.954	0.13
500	22.50	0.0274	0.764	0.23
750	23.63	0.0393	1.043	0.10

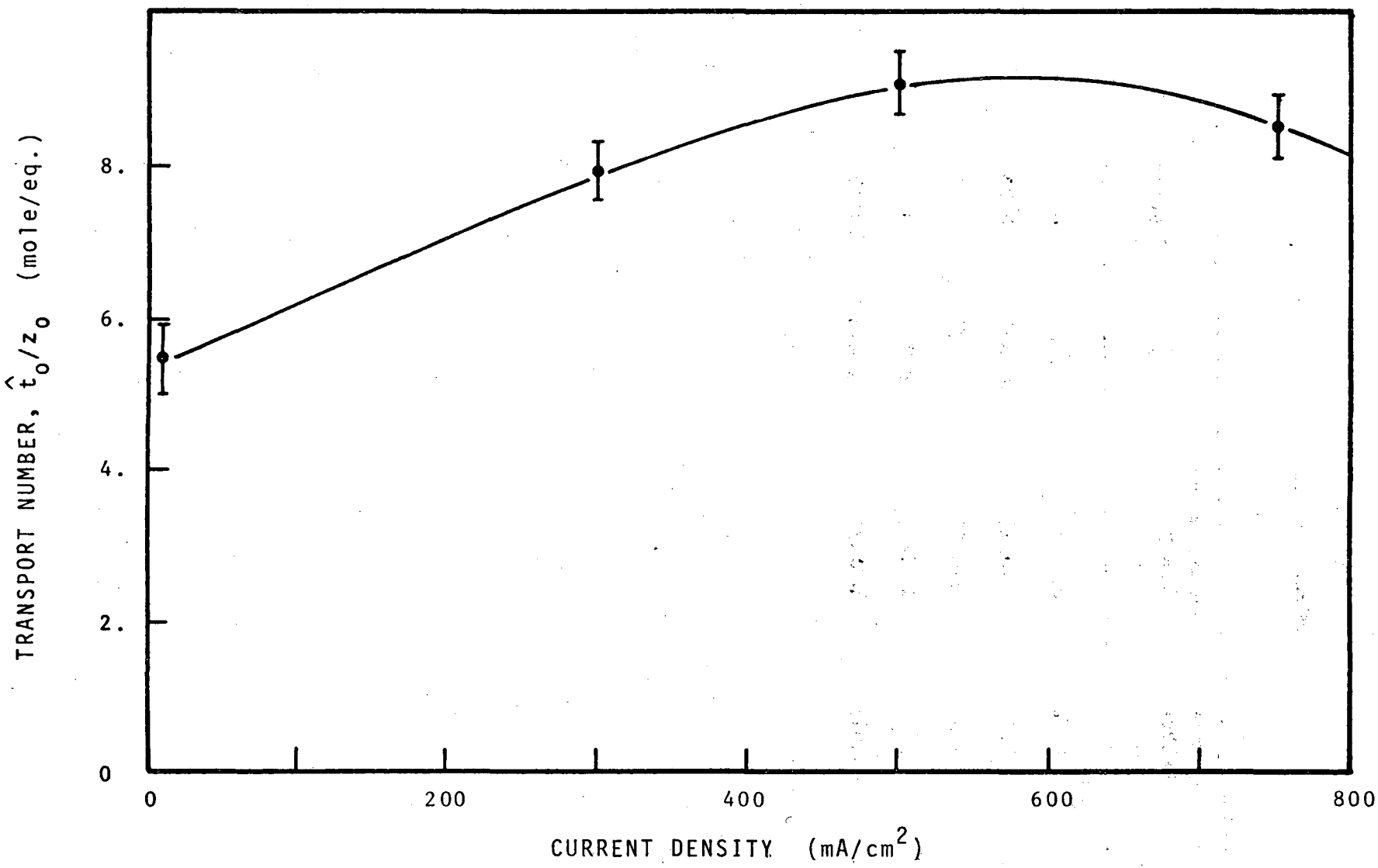

Fig. 2. Water transport number results obtained with radiotracers. Nafion membrane in 0.1 N NaCl solution, at 27°C.

Table of Contents

Summary ii

Introduction. 1

Theory 1

Apparatus 5

Transport Cell 5

Procedure 8

Results 16

Discussion 25

Conclusions 34

Acknowledgment 34

Nomenclature 35

References 36

Appendix A 37

Appendix B 43

INTRODUCTION

Transport properties of ion exchange membranes have been studied for many years; recent improvements in membranes have sparked increased interest in this field. A question of practical interest is how the selectivity of Nafion membranes changes as the current density increases. Several studies have reported on the dependence of transference numbers on current density (6 - 10). Also, studies have been made of the water transport number as a function of current density (11 - 13). Changes in transport numbers with current density were attributed to the effects of concentration changes produced within thin diffusion layers adjacent to the membranes. The present work is an evaluation of transport numbers for Nafion membranes immersed in 0.1 N NaCl solution. The effects of concentration polarization have been minimized by vigorous stirring of the solutions adjacent to the membrane. The range of current densities studied here was extended to 750 mA/cm^2, about an order of magnitude higher than previously reported.

Radiotracer methods have been used to determine the transport numbers of both sodium and water through an 1100 equivalent weight Nafion membrane. Each transport number was obtained by determining the change in tracer flux through the membrane at the moment current began to flow. The theory and experimental methods used were similar to those described by Meares and Sutton (1).

THEORY

The radiotracer transport theory discussed here is based on multicomponent transport equations presented by Newman (14), and the notation reflects this origin. A similar development has been presented by Meares and Sutton (1), and Sutton (15). The present work is a reformulation of the concepts presented by Meares and Sutton with a somewhat different emphasis. Equations similar to these presented below have also been derived from an irreversible-thermodynamics point of view by Miller (16, 17).

The transport equations are derived for the membrane phase assuming no gradients in chemically-distinct species. Of course, gradients in radioisotopes are considered. The membrane has been chosen as the reference species with zero velocity. The basic diffusional flux equations can be written

$$N_j = -C_j \sum_k L^m_{jk} C_k \nabla\mu_k \tag{1}$$

The superscript m indicates the membrane phase. The gradient in chemical potential is:

$$\nabla\mu_k = RT\nabla\ell n\, C_k + z_k F \nabla\phi \tag{2}$$

where the activity coefficient term has been dropped from Eq. 2 because the only concentration gradients are among radioisotopes.

Substituting Eq. 2 into Eq. 1 yields

$$N_j = -RTC_j \sum_k L^m_{jk} \nabla C_k - \frac{t^m_j}{z_j}\frac{\kappa}{F}\nabla\phi \tag{3}$$

Also:

$$i = -\kappa\nabla\phi \tag{4}$$

Substitution of Eq. 4 into Eq. 3 yields

$$N_j = -RT\, C_j \sum_k L^m_{jk} \nabla C_k + \frac{t^m_j}{z_j}\frac{i}{F} \tag{5}$$

Now consider an example system consisting of 2 positive ions + and *, one anion, -, a neutral solute, o, and the membrane. The positive ions are assumed to have identical chemical and transport properties. We consider the interdiffusion of + and *.

$$N_+ = -N_* \tag{6}$$

$$N_- = 0 \tag{7}$$

$$N_o = 0 \tag{8}$$

$$\nabla C_+ = -\nabla C_* \tag{9}$$

$$\nabla\phi = 0 \tag{10}$$

$$\nabla C_- = 0 \tag{11}$$

Substitution of Eqs. 9 - 11 into Eqs. 6 - 8 yields:

$$L_{o+} = L_{o*} \tag{12}$$

$$L_{-+} = L_{-*} \tag{13}$$

$$L_{++} C_+ + L_{+*}C_* = L_{**}C_* + L_{+*}C_+ \tag{14}$$

The transport number of species j is defined as:

$$\frac{t_j^m}{z_j} = \frac{C_j F^2}{\kappa} \sum_{k \neq m} L_{jk} z_k C_k \tag{15}$$

Substitution of Eqs. 12 - 14 into Eq. 15 yields:

$$\frac{t_*^m}{z_* C_*} = \frac{t_+^m}{z_+ C_+} \tag{16}$$

Equation 15 can be used to determine t_+^m/z_+ or the total cation transference number once t_*^m/z_* is known. In general, t_*^m/z_* is a function of C_*, but

$$\frac{\hat{t}_+}{z_+} = \frac{(t_*^m + t_+^m)}{z_+} \tag{17}$$

$$= (1 + C_+/C_*) \frac{t_*^m}{z_*} \tag{18}$$

$$= \frac{C_* + C_+}{C_*} \frac{t_*^m}{z_*} \tag{19}$$

$$C_+ + C_* = C_m \tag{20}$$

In the following discussion C_m will be assumed to be constant.

Now consider the flux of radiotracer species.

$$N_* = -RTC_* (L_{**} \nabla C_* + L_{*+} \nabla C_+) + \frac{t_*^m}{z_*} \frac{i}{F} \tag{21}$$

In all cases we will consider Eq. 9 to hold. Therefore:

$$N_* = -RTC_* (L_{**} - L_{*+}) \nabla C_* + \frac{t_*^m}{z_*} \frac{i}{F} \tag{22}$$

The quantity $RTC_* (L_{**} - L_{*+})$ is the tracer interdiffusion coefficient, D_*. It is assumed that D_* is a constant over the concentration range of C_* encountered in the experiments. Helfferich (18) and Meares and Sutton (1) consider D_* to be a constant.

Substitution of Eqs. 19 and 20 into Eq. 22 yields:

$$N_* = -D_* \nabla C_* + \frac{\hat{t}_+ C_*}{z_+ C_m} \frac{i}{F} \tag{23}$$

Equation 23 is a differential equation in C_* which has the general form

$$\nabla C_* + \alpha C_* = \beta \tag{24}$$

where α and β are constants, when N_* and i are constant across the membrane.

Equation 24 can be integrated with $C_* = C_{*1}$ on side 1, and $C_* = C_{*2}$ on side 2 of the membrane. The result can be used in Eq. 23 to yield:

$$N_* = - \frac{(C_{*2} - C_{*1} e^{-\alpha\delta})\alpha D_*}{(1 - e^{-\alpha\delta})} \tag{25}$$

where $\alpha = - \dfrac{\hat{t}_+ \, i}{z_+ \, F \, D_* \, C_m}$ (26)

Equation 25 is quite general provided the previously-mentioned assumptions are satisfied, but it is not convenient to use when i = 0. When i = 0, $\alpha = 0$ and Eq. 25 is undetermined. However, it is easy to perform an integration of Eq. 23 in this case. If we designate N_*^o to signify the tracer flux with current equal to zero and N_*^i to indicate the tracer flux with non-zero current, then Eq. 25 applies to N_*^i and

$$N_*^o = -D_* \frac{(C_{*2} - C_{*1})}{\delta} \tag{27}$$

Equations 25 and 27 are two equations in 2 unknowns, α and D_*. One convenient equation derived from Eqs. 25 and 27 is

$$\frac{N_*^i}{N_*^o} = \frac{\alpha\delta}{(1 - e^{-\alpha\delta})} \frac{(C_{*2}/C_{*1} - e^{-\alpha\delta})}{(C_{*2}/C_{*1} - 1)} \tag{28}$$

APPARATUS

Transport Cell

The basic configuration of the transport cell is shown in Fig. 3. For clarity only the primary features of the cell have been illustrated. Each cell compartment contains its own centrifugal pump. The pumps are each driven through a magnetic coupling to an external, variable-speed drive motor. The internal volume of each pump chamber is about 13 mℓ. The exposed membrane area is 0.075 cm^2, and the working electrode geometric area is 25.6 cm^2. The cell is constructed of Plexiglas. Not shown in the figure are and sampling and manometer ports. The sampling ports enter the conical annulus at the point where the fluid enters the annulus from the pumping chamber. The manometer port enters the conical annulus about 1 cm upstream from the center of the membrane. The flow chamber is about 6.4 cm in diameter, and the plane of the membrane is about 1.5 cm from the plane of the working electrode.

Mixing-time experiments were performed which showed that the cell fluid was completely mixed in less than 70 ms. Small volumes of concentrated salt solution were injected into the flow channel and the bulk solution conductivity was recorded on a Tektronix Model 564 storage oscilloscope. Assuming that 70 ms represents the residence time for one cell-volume of fluid, the volumetric flow rate is about 185 mℓ/s. This flow rate corresponds to a velocity of about 25 m/s in the central flow channel returning fluid to the pump. At the top of the conical annulus the velocity is calculated to be about 4.4 m/s. The diameter of the central channel is 0.31 cm, and the conical flow channel is about 0.043 cm thick. Thus the Reynolds numbers range from about 2.2×10^3 to 9.0×10^4.

Two different types of working electrodes were used: smooth silver sheets and porous silver. The smooth silver-sheet electrodes were used at low current densities. The cathode was anodized, prior to each experiment, until about 15 C of silver chloride was formed. A freshly polished anode was used in each of the low-current-density experiments. The porous silver electrodes were used in high-current-density experiments. Prior to use, one of the electrodes was anodized to a silver chloride capacity of about 200 C. Thereafter this electrode was used as the cathode, without further anodizing, for all

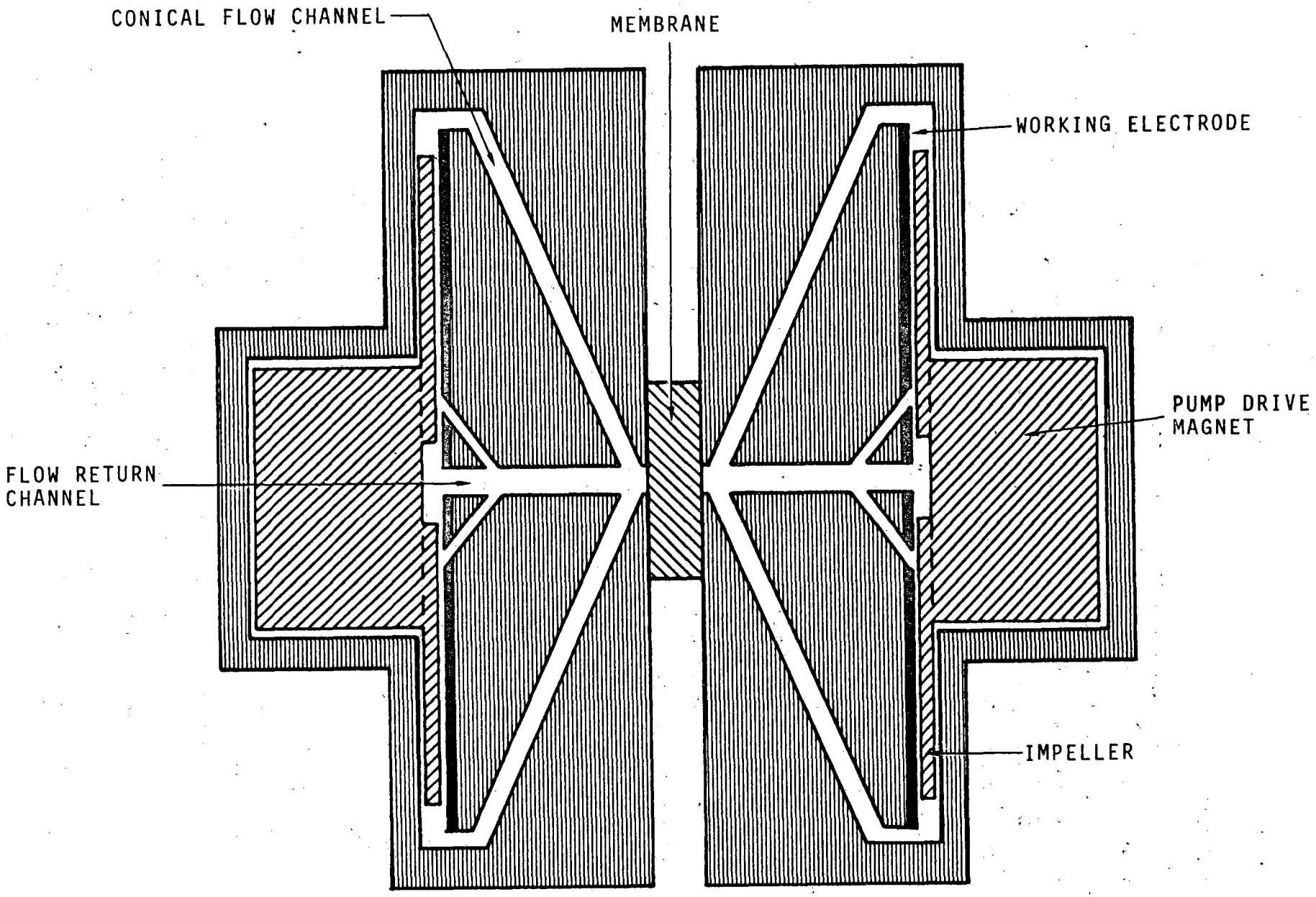

Fig. 3. Transport cell.

high-current-density experiments. The porous silver anode accumulated silver chloride during each experiment, but the silver chloride was not removed between experiments because the total charge passed during the experiments never approached the electrode's capacity. After each experiment, both porous silver electrodes were rinsed with distilled water. They were then stored in covered petri dishes until the next experiment.

Reference electrodes were connected to each compartment of the transport cell through the manometer tubes. Anodized silver wires were inserted into the manometer tubes through rubber septums. Radiotracer results showed that no mixing occurred between the chamber fluid and the fluid in the manometer tubes.

A single specimen of Nafion 7-1100 was used. The specimen was cut from the same sheet used by Pintauro (19). (Approximately three years have passed since Pintauro completed his work.) The nominal equivalent weight of the membrane was 1100 g/eq. Pintauro determined the ion exchange capacity of the original sheet by a pH titration method. He found a capacity of 0.851×10^{-3} eq/g dry membrane. The radiotracer method used in the present work gave a value of 0.881×10^{-3} eq/g dry membrane (4). The nominal ion exchange capacity, based on the equivalent weight, is 0.909×10^{-3} eq/g dry membrane. Prior to the first radiotracer experiment of the present work, the Nafion specimen was boiled in distilled water for 30 minutes. Thereafter it was maintained in a solution of 0.1 N NaCl at room temperature ($\approx 22°C$) except during experiments.

All radiotracer-free solutions used in the present work were made from Baker reagent grade, ACS-specification salts and distilled water. Radiotracers were obtained from commercial sources as aqueous salt solutions or as tritiated water. Final dilution of the tracer solutions was performed in this laboratory. Certified reference solutions obtained from commercial sources were used to prepare radiotracer standards. All experiments were conducted in 0.100 N NaCl solution.

PROCEDURE

Each experiment was conducted with the objective of maintaining constant circulation velocities and a constant pressure difference across the membrane. As will be seen, these two requirements were mutually exclusive with the apparatus used. The following compromise procedure was adopted as a standard.

First the cell was prepared, and the desired working electrodes were mounted in place. Smooth silver-plate electrodes were used for membrane current densities less than 300 mA/cm^2, and porous silver electrodes were used at 300 mA/cm^2 and above. The cathode was previously anodized to a total charge greater than 15 C. When the cell was ready, the Nafion membrane was mounted between the two solution compartments. A single Nafion specimen was used in all five experiments. Current was always passed through the same portion of the specimen, and the membrane was always mounted with the same side facing the cathode.

After the membrane was mounted, the cell was filled with 0.1 N NaCl solution containing no radiotracers. This solution concentration was chosen for this series of demonstration experiments in order to minimize possible complications caused by nonideality and concentration gradients. Equation 20 is expected to be a good approximation at this concentration. The filled cell was mounted in the drive assembly, and each solution compartment was connected to an open-ended mercury-filled manometer. All air was purged from the manometer lines by injecting additional 0.1 N salt solution into the cell chamber with a syringe. When the purging procedure was complete, freshly anodized silver-silver chloride reference electrodes were placed into the salt solution in each manometer line. These reference electrodes were thin wires which were inserted into the manometer lines through rubber septums. The voltage between the reference electrodes was measured with a Keithley Model 616 electrometer. The temperature was determined with a copper-contantan thermocouple placed in a well in the cell body. The thermocouple was located about 2.5 cm from the center of the membrane, but it was only 4 mm from the well-stirred solution in the chamber. The thermocouple voltage was amplified with an Omega omni-amp-IIB amplifier equipped with an ice-point reference junction, and the amplifier output was recorded on a Hewlett Packard Model 7132A strip chart recorder. Fig. 4 shows a schematic representation of the basic experimental apparatus.

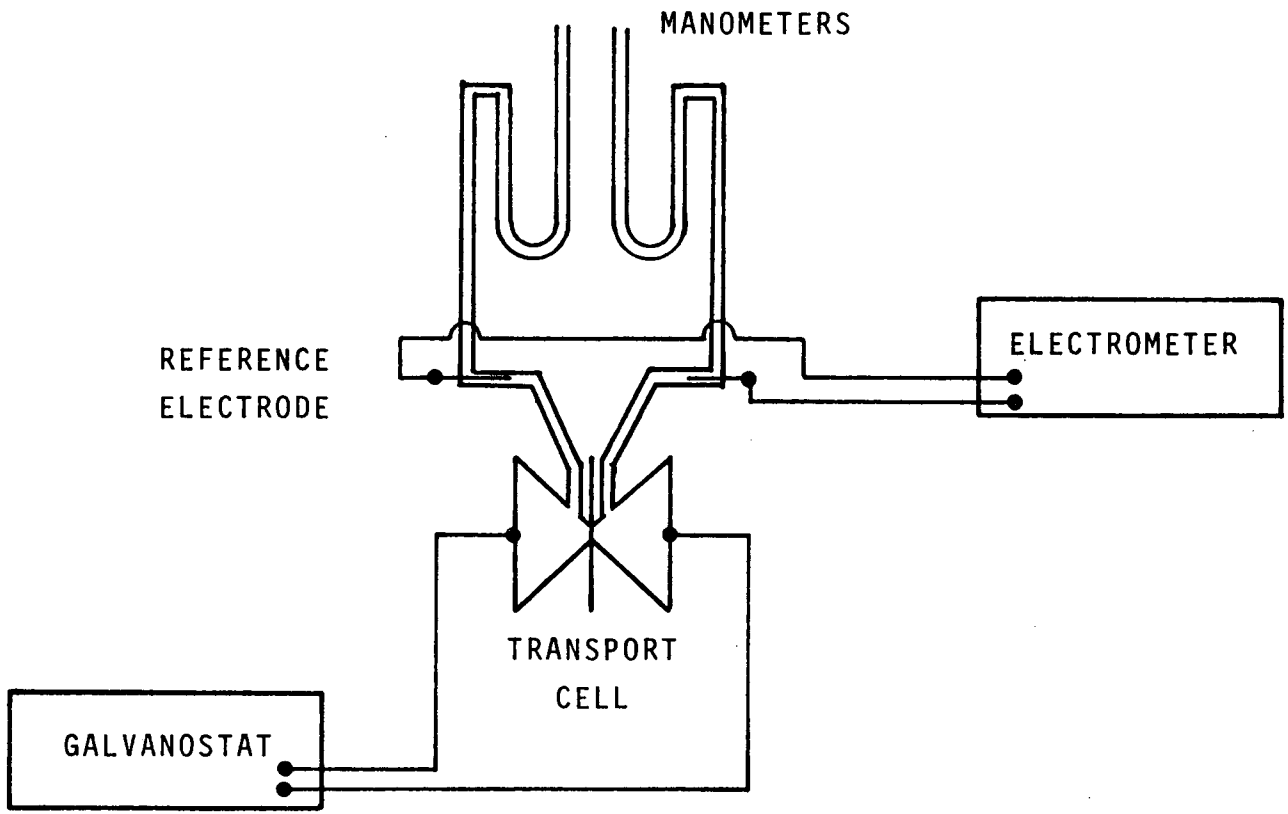

Fig. 4. Transport cell and electrical apparatus.

Next, the stirring motors were started and the speeds were adjusted until zero pressure differential existed across the membrane. The pressure history of each experiment is presented in Appendix A. The motors were allowed to run at relatively high speed until the thermocouple temperature reached about 25°C. Then the speeds were reduced to the operating range, and the temperature was allowed to stabilize. Throughout this pre-radiotracer period the pressure difference across the membrane was maintained as close to zero as possible.

When the temperature had stabilized, the motors were stopped and radiotracers were injected into the solution on the anode side of the membrane, designated side 1. The solution on side 2 would eventually become the catholyte. About 1 mℓ of 0.1 N NaCl solution containing high concentrations of radiotracers was injected through a rubber septum with a syringe. This addition of solution raised the level of the manometer and consequently created higher pressure on side 1. The pressure was equalized by the addition of a similar volume of the original, tracer-free, solution to side 2. Then the stirring motors were started, and the speeds were again adjusted to maintain a near-zero pressure difference across the membrane.

After the radiotracers had been injected, 10 μℓ samples of solution were periodically withdrawn from both sides of the cell. The samples were obtained with Hamilton syringes equipped with Chaney adaptors. Sampling was continued in this manner for about three hours. As samples were taken, the levels of the manometers changed. The manometer levels were constantly monitored throughout the experiment. From this data volume changes in each compartment could be determined. The motor speeds were occasionally changed in order to minimize the pressure differential across the membrane. Changes in motor speed had no effect on the observed manometer levels. This first period when no current was flowing was termed the self-diffusion period.

Following the self-diffusion period, a constant current was made to flow through the membrane. The current was controlled with a Princeton Applied Research, model 173, potentiostat operated in the galvanostatic mode. During the experiment conducting 750 mA/cm^2 of current, a 50 V regulated power source was placed in series with the counter electrode to increase the compliance

voltage of the Princeton Applied Research potentiostat. Immediately prior to application of the current, three radiotracer samples were taken from the solutions on each side of the membrane, and the motor speeds were adjusted. While the current was flowing, samples were withdrawn only from side 2, and the motor speeds remained constant. The period during which current flowed was designated as the electrodialysis period.

Immediately following cessation of current, three radiotracer samples were withdrawn from each cell compartment and the motor speeds were adjusted. Thereafter samples were withdrawn periodically for about one hour. This third period was designated the dialysis period.

Following the dialysis period, the experiment was terminated. The termination procedure involved withdrawing three radiotracer samples from each manometer line near where it was attached to the transport cell. Then the lines were clamped shut and disconnected from the manometers. The cell was removed from the drive-motor assembly, and the contents of each compartment were withdrawn with a syringe. The recovered cell contents were weighed and stored in clean glass bottles. The cell was then disassembled. The membrane was stored in approximately 500 mℓ of constantly stirred 0.1 N NaCl solution. Each half cell was individually leached in separate volumes of distilled water for about 24 hours. They were then dried with methanol and reassembled for the next experiment.

Three samples of each of the recovered cell solutions were taken for radiotracer analysis. The pH of each cell solution and the original 0.1 N salt solution was determined. Then 10 mℓ samples were titrated to determine the chloride concentration in each of the three solutions. Silver nitrate was used as titrant, and the end point was determined with an Orion Model 94-16 silver sulfide electrode. The reference electrode was an Orion Model 90-02 double junction electrode. Sodium ion transference numbers were calculated from the titration results according to the formula:

$$t_+ = \frac{z_+ F \Delta C V}{2q} \tag{29}$$

The radiotracer samples were analyzed by liquid scintillation spectroscopy. The 10 μℓ aqueous samples were added to 10 mℓ of Aquassure scintillation cocktail. A Hewlett-Packard Model 2002 scintillation spectrometer was used to count the samples. Standards were prepared from certified calibration solutions purchased from commercial sources.

The objective of the experimental procedure was to allow an accurate determination of each radiotracer flux immediately prior to and following the commencement of current. The flux was easily related to the observed rate of activity increase in the side 2 solution, but the experiment is never truly at steady-state because the cell volumes were constant. Figure 5 is a qualitative representation of how the side 2 activity changes with time. The solid lines represent experimental data with exaggerated curvature. The required flux ratio N_*^i/N_*^o, Eq. 28, must be based on the tangents of the two solid curves at the moment current is applied (the dashed lines). Because of statistical scatter in the scintillation counting technique, accurate slopes of the tangent lines are difficult to obtain directly from the experimental curves. Therefore, the following procedure was developed to determine the quasi-steady state fluxes at the instant current flow began.

First the data were plotted as side 2 activity versus time. Figure 6 shows typical experimental data for sodium ion transport during the self-diffusion and electrodialysis periods. (Table 2 in the results section lists statistical data for other experiments.) A least-squares straight line was then constructed through the data obtained during each period, as shown. An average flux for each period was then calculated from the slope of the appropriate straight line. The average flux for the self-diffusion period was given the symbol F_*^o, and F_*^i was used to designate the flux during the electrodialysis period. Then a correction factor was applied to both F_*^o and F_*^i to obtain the required fluxes N_*^o and N_*^i respectively.

The correction factor for the self-diffusion period was derived for a system in which the tracer diffuses from a compartment at high concentration, C_1, into a compartment at low concentration, C_2. The compartments are assumed to be of constant volumes V_1 and V_2, and the rate of diffusion is controlled by a membrane of constant thickness and permeability. Thus

$$N_* = -\frac{P_* (C_2 - C_1)}{\delta} \tag{30}$$

It is also assumed that the membrane area and starting concentrations in each compartment are known. Based on this model it is a simple matter to determine that

$$(C_2 - C_2^o) = \left(\frac{n}{V_1 + V_2} - C_2^o\right)(1 - e^{-\gamma t}) \tag{31}$$

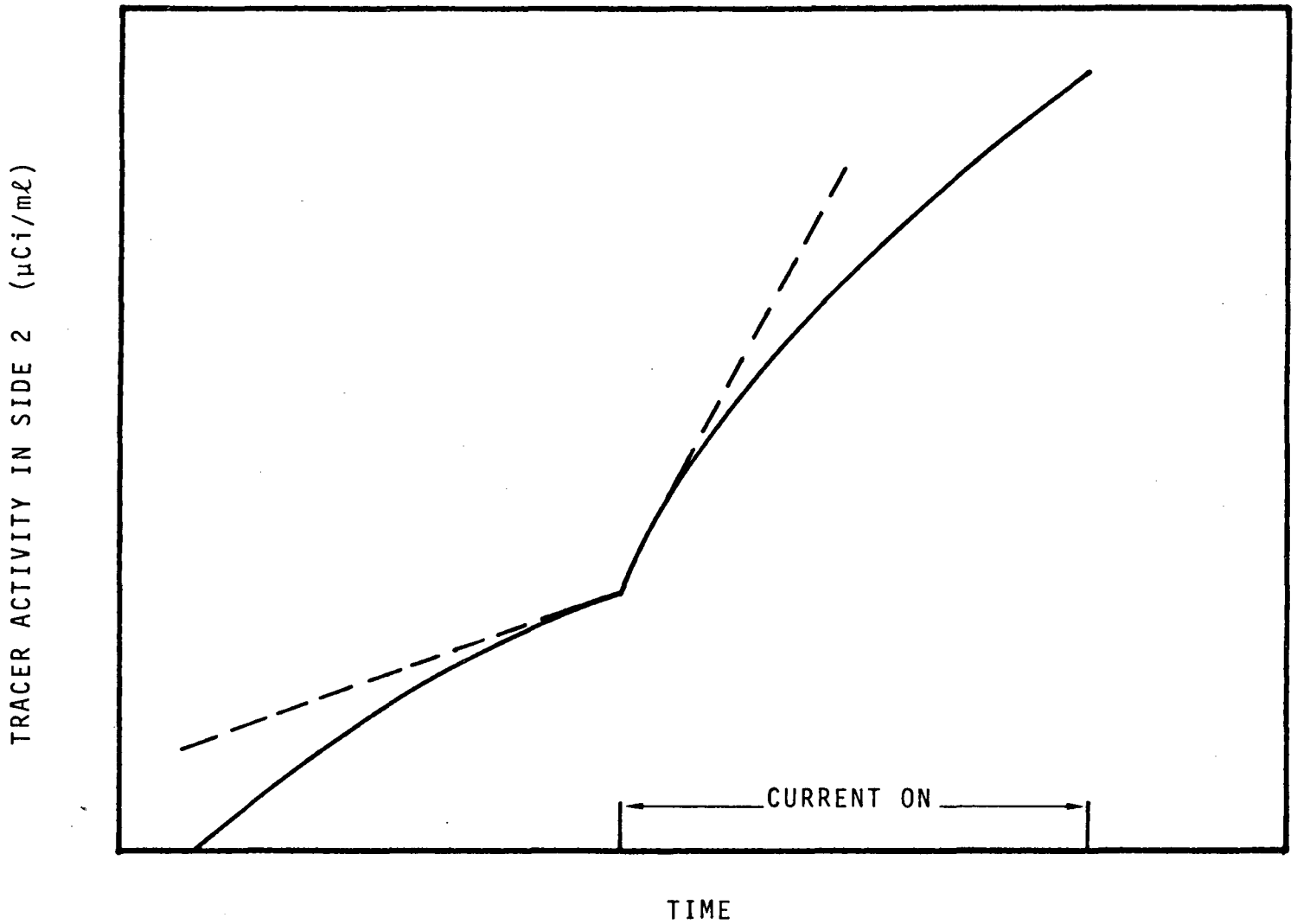

Fig. 5. Qualitative experimental data (solid curves) showing exaggerated curvature resulting from non-steady-state conditions. Dashed lines represent tangents to the experimental data at the moment current is applied.

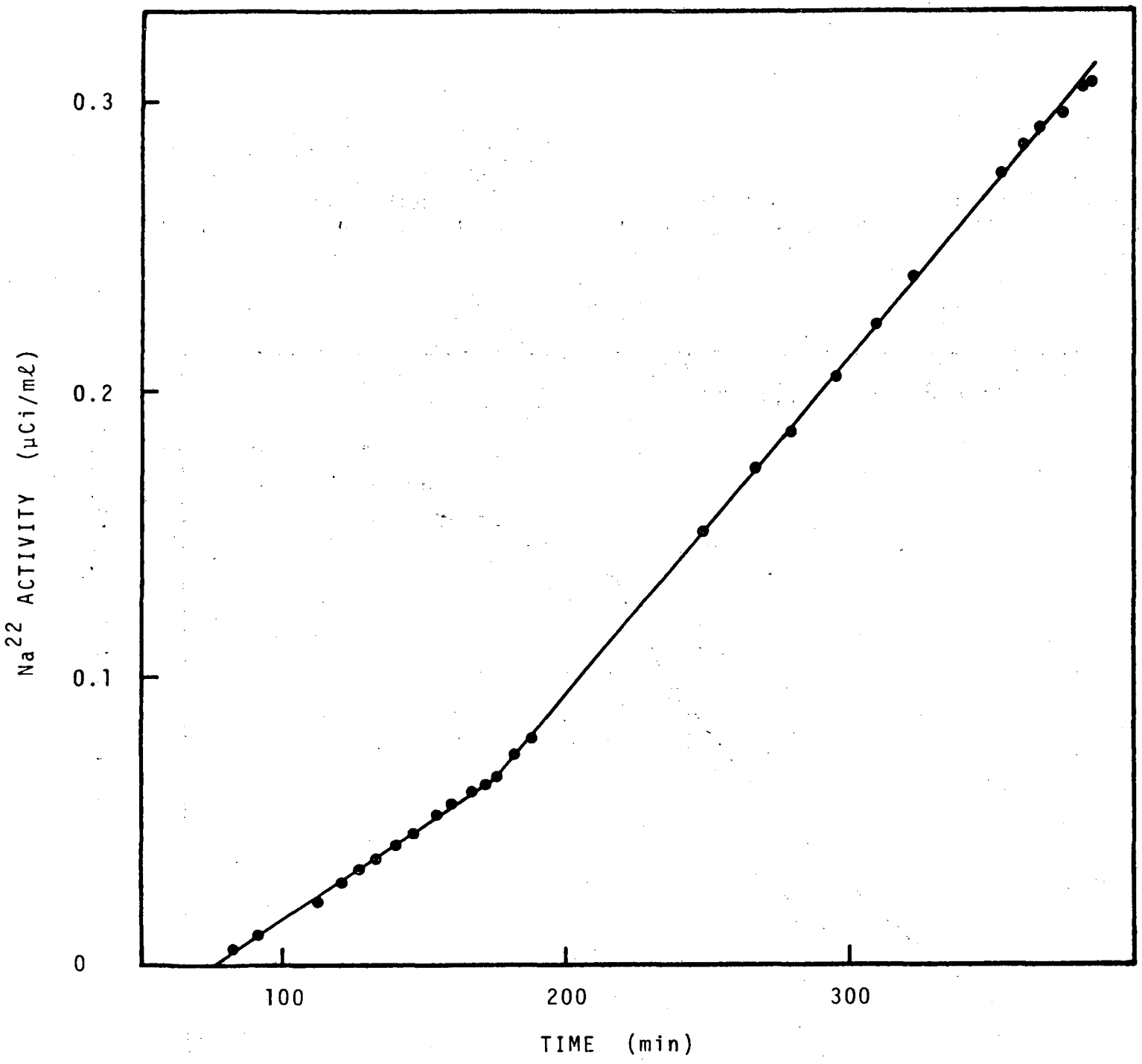

Fig. 6. Sodium ion tracer buildup in the solution on side 2. Current turned on at 175 minutes. Current density = 10 mA/cm^2.

where C_2^o is the concentration at t = 0 on side 2, and n is the total quantity of tracer in both compartments. Gamma is the reciprocal of the time constant for the experiment, $\gamma = PA/\delta V$, where A = the membrane area, and $V = V_1V_2/(V_1 + V_2)$.

A similar equation is obtained for the concentration change on side 1. The flux at any time is described by

$$N_* = -\frac{P_*}{\delta}(C_2^o - C_1^o)e^{-\gamma t} \tag{32}$$

The ratio of the flux at time t to the average flux over the time interval from zero to t can now be determined.

$$\frac{N_t}{N_{ave}} = \frac{\gamma t}{e^{\gamma t} - 1} \tag{33}$$

This expression can be rewritten in terms of the observed concentrations.

$$\frac{N_t}{N_{ave}} = \frac{\ln\left[\dfrac{\dfrac{n}{V_1 + V_2} - C_2^o}{\dfrac{n}{V_1 + V_2} - C_2}\right]}{\left[\dfrac{C_2 - C_2^o}{\dfrac{n}{V_1 + V_2} - C_2}\right]} \tag{34}$$

Equation 33 has been used to obtain values of N_*^o from the "average" fluxes F_*^o. Both fluxes are tablulated in the Results section.

A similar line of logic was used to obtain the correction factor for the electrodialysis period, except in this case the flux was assumed to be proportional to the concentration of tracer in the "donating" compartment, i.e., side 1.

$$N_* = -P_* C_1 \alpha \tag{35}$$

where α is defined in Eq. 24. This equation is satisfactory for $\alpha\delta$ less than about -5. For larger $\alpha\delta$ a more complicated equation such as Eq. 25 must be used. In all cases an exponential dependence of the concentration and the flux will be obtained, but the coefficients will vary.

If Eq. 35 is used to obtain the correction factor, the results are:

$$(C_2 - C_2^o) = \left(\frac{n}{V_2} - C_2^o\right)(1 - e^{-\varepsilon t}) \tag{36}$$

where $\varepsilon = -\dfrac{A\,P_*\alpha}{V_1}$

$$\frac{N_t}{N_{ave}} = \frac{\varepsilon t}{(1 - e^{-\varepsilon t})} \tag{37}$$

$$\frac{N_t}{N_{ave}} = \frac{\ln \left[\dfrac{\frac{n}{V_2} - C_2^o}{\frac{n}{V_2} - C_2} \right]}{\left[\dfrac{C_2 - C_2^o}{\frac{n}{V_2} - C_2^o} \right]} \tag{38}$$

Equation 38 was used to correct the average flux in the electrodialysis period F_*^i to obtain N_*^i. The corrected fluxes, N_*^o and N_*^i, were then used in Eqs. 27 and 28 to obtain D_* and $\alpha\delta$. The results were tabulated in terms of P_* which is merely the product of D_* and the dimensionless solubility of the tracer in the membrane. The following solubilities have been used:

$$S_{Na^+} = 10.9 \quad (4, 19) \tag{39}$$

$$S_{H_2O} = 0.295 \quad (19) \tag{40}$$

RESULTS

Typical experimental results showing how the sodium-22 activity in the solution on side 2 changes with time are presented in Fig. 6. The results of all five experiments with current densities between 10 mA/cm^2 and 750 mA/cm^2 are listed in Tables 2 through 10. Table 2 shows the chember volumes and average temperature during both the self-diffusion and electrodialysis periods. The total quantity of each radiotracer is given in micro Curies. The chamber volumes depend on which working electrodes were employed. Porous silver working electrodes were used for current densities of 300 mA/cm^2 and above. Table 3 shows the slopes and coefficients of determination of the straight lines used to calculate the F_* fluxes.

Table 4 shows the Hittorf results. The chloride ion concentration was determined by titration with $AgNO_3$, and the transference numbers were calculated according to Eq. 29.

Table 2

i (mA/cm^2)	Total Radiotracer Na^{22} (μCi)	Total Radiotracer H^3 (μCi)	Chamber Volume side 1 (mℓ)	Chamber Volume side 2 (mℓ)	Average Temperature T_{SD} (°C)	Average Temperature T_E (°C)
10	33.10	364.1	12.9	12.8	25.8	25.7
100	14.31	53.2	12.9	12.8	27.0	27.2
300	32.13	311.5	13.0	13.0	28.1	28.1
500	20.62	325.5	13.0	13.0	26.9	26.6
750	32.83	305.6	13.0	13.0	26.0	26.7

Table 3

i	Self-Diffusion Period				Electrodialysis Period			
	Na^{22}		H^3		Na^{22}		H^3	
	slope	R^2	slope	R^2	slope	R^2	slope	R^2
(mA/cm^2)	($\mu Ci/m\ell$-min)		($\mu Ci/m\ell$-min)		($\mu Ci/m\ell$-min)		($\mu Ci/m\ell$-min)	
10	6.571×10^{-4}	0.9992	8.736×10^{-4}	0.9987	1.166×10^{-3}	0.9996	9.207×10^{-4}	0.9978
100	2.874×10^{-4}	0.9971			3.882×10^{-3}	0.9997	2.920×10^{-4}	0.9736
300	5.67×10^{-4}	0.9990	6.876×10^{-4}	0.9984	2.247×10^{-2}	0.9984	3.719×10^{-3}	0.9659
500	3.515×10^{-4}	0.9992	6.961×10^{-4}	0.9976	2.399×10^{-2}	0.9997	7.337×10^{-3}	0.9940
750	5.46×10^{-4}	0.9984	7.06×10^{-4}	0.9950	5.532×10^{-2}	0.9986	9.559×10^{-3}	0.9821

Table 4

Hittorf Results (Cl^- Titration)

i (mA/cm^2)	Charge Passed (C)	Concentration Change (M)	$\hat{t}_+$
10	9.54	0.0184	1.196
100	15.75	0.0228	0.898
300	17.55	0.0267	0.954
500	22.50	0.0274	0.764
750	23.63	0.0393	1.043
		Ave	0.971 ± 0.161

Tables 5 and 8 show the radiotracer activities at various times during each experiment. The initial activity is immediately following injection of tracer into side 1. Also shown are the activities in both compartments at the moment when the current began to flow, and the moment when current flow ceased.

Tables 6 and 9 show the calculated fluxes obtained in each experiment. The fluxes were calculated from the rate of increase of radiotracers in the side 2 chamber. Each F_* flux is based on the slope of a least-squares straight-line fit of the data. F_*^o was obtained during the self-diffusion period, and F_*^i represents the average flux during the electrodialysis period. N_*^o represents the tracer flux immediately prior to current flow, and N_*^i represents the flux immediately following the commencement of current. N_*^o was calculated using Eq. 34 (Procedure section), and N_*^i was obtained with Eq. 38.

Tables 7 and 10 illustrate the permeability and transference-number results obtained with radiotracers.

Table 11 shows the pH values obtained before and after each experiment.

Table 5

Na^{22} Radiotracer Activities

i (mA/cm^2)	Initial Activity side 1 ($\mu Ci/m\ell$)	Activity at End of Self-Diffusion Period side 1 ($\mu Ci/m\ell$)	Activity at End of Self-Diffusion Period side 2 ($\mu Ci/m\ell$)	Activity at End of Electrodialysis Period side 1 ($\mu Ci/m\ell$)	Activity at End of Electrodialysis Period side 2 ($\mu Ci/m\ell$)
10	2.56	2.50	0.066	2.25	0.313
100	1.11	1.06	0.052	0.923	0.187
300	2.47	2.35	0.123	2.06	0.413
500	1.59	1.52	0.070	1.28	0.305
750	2.53	2.41	0.120	2.02	0.503

Table 6

Na^{22} Radiotracer Fluxes

i (mA/cm^2)	F_*^o ($\mu Ci/(cm^2 \cdot s)$)	F_*^i ($\mu Ci/(cm^2 \cdot s)$)	N_*^o ($\mu Ci/(cm^2 \cdot s)$)	N_*^i ($\mu Ci/(cm^2 \cdot s)$)
10	1.87 E - 3	3.32 E - 3	1.82 E - 3	3.50 E - 3
100	8.17 E - 4	1.10 E - 2	7.77 E - 4	1.18 E - 2
300	1.64 E - 3	6.49 E - 2	1.56 E - 3	6.93 E - 2
500	1.01 E - 3	6.93 E - 2	9.64 E - 4	7.53 E - 2
750	1.58 E - 3	1.60 E - 1	1.50 E - 3	1.74 E - 1

Table 7

Na^{22} Radiotracer Results

i (mA/cm^2)	Permeability Coefficient (cm^2/s)	$-\alpha\delta$	$\hat{t}_+$
10	2.17 E - 5	1.431	1.034
100	2.25 E - 5	14.35	1.074
300	2.02 E - 5	42.18	0.956
500	1.93 E - 5	74.50	0.959
750	1.90 E - 5	110.4	0.934
	Ave (2.05 ± 0.15)E - 5		Ave 0.991 ± 0.060

Table 8

H^3 Radiotracer Activities

i (mA/cm^2)	Initial Activity side 1 (μCi/mℓ)	Activity at End of Self-Diffusion Period side 1 (μCi/mℓ)	Activity at End of Self-Diffusion Period side 2 (μCi/mℓ)	Activity at End of Electrodialysis Period side 1 (μCi/mℓ)	Activity at End of Electrodialysis Period side 2 (μCi/mℓ)
10	28.20	28.13	0.075	27.93	0.272
100	4.12	4.11	0.008	4.10	0.018
300	23.96	23.83	0.129	23.78	0.177
500	25.04	24.92	0.125	24.84	0.198
750	23.50	23.37	0.126	23.31	0.195

Table 9

H^3 Radiotracer Fluxes

i (mA/cm^2)	F_*^o (μCi/(cm^2·s))	F_*^i (μCi/(cm^2·s))	N_*^o (μCi/(cm^2·s))	N_*^i (μCi/(cm^2·s))
10	2.48 E - 3	2.62 E - 3	2.48 E - 3	2.63 E - 3
100		8.30 E - 4		8.31 E - 4
300	1.99 E - 3	1.07 E - 2	1.98 E - 3	1.08 E - 2
500	2.01 E - 3	2.12 E - 2	2.00 E - 3	2.12 E - 2
750	2.04 E - 3	2.81 E - 2	2.03 E - 3	2.81 E - 2

Table 10

H^3 Radiotracer Results

(mA/cm^2)	Permeability Coefficient (cm^2/s)	$-\alpha\delta$	$\hat{t}_o/z_o$ (mole/eq)
10	2.55 E-6	0.116	5.45
100			
300	2.40 E-6	5.39	7.95
500	2.33 E-6	10.55	9.05
750	2.51 E-6	13.78	8.51
	Ave (2.45 $\pm$ 0.10)E-6		

Table 11

pH Data

i (mA/cm^2)	Side 1 (Anode)		Side 2 (Cathode)	
	Initial pH	Final pH	Initial pH	Final pH
10	5.9	6.5	5.9	6.7
100		6.7	5.8	6.8
300	7.5	7.4	6.1	9.2
500	6.2	7.3	6.0	7.2
750	6.6	7.4	5.7	10.2

DISCUSSION

The permeability and transference-number results obtained with radiotracers are illustrated in Table 7 and 10. The Hittorf results are shown in Table 4. Both the Hittorf and radiotracer results for sodium transport show moderate scatter. Systematic and statistical errors contributing to the experimental uncertainty will now be considered.

There are two sources of potentially significant and systematic error: temperature fluctuations and mass-transfer effects. The average temperatures obtained during the experiments are given in Table 2. The largest temperature fluctuation in any experiment occurred when $i = 100\ mA/cm^2$ and was 3.2°C. The average temperature fluctuation was 2.2°C. Thus, the average temperatures listed in Table 2 are subject to an error of approximately $\pm$ 1°C. This is the same magnitude as the standard deviation of the average temperatures listed in Table 1. Therefore, in the following discussion it is assumed that all experiments were conducted at an average temperature of $\approx$27°C. Better temperature control can be expected to reduce the overall scatter of the experimental results.

The second source of systematic error is the possibility that mass-transfer boundary layers exist at the membrane-solution interface. Experimental evidence suggests that boundary layers were not important in these experiments, but some results were ambiguous. Two tests were performed to determine the approximate thickness of the boundary layer adjacent to metal electrodes that were used in place of the Nafion membrane. The current-limiting plateaus were present in both tests, but the results of silver plating experiments did not agree with results obtained using the quinone-hydroquinone couple. As a result of this conflict an attempt was made to determine the limiting current using a Nafion membrane in 0.01 N NaCl solution. No limiting current was obtained at the current densities investigated, up to 116 mA/cm^2. Higher current densities were not tested because of limitations on the compliance voltage available with the galvanostat. Considering this body of evidence as a whole, it was concluded that the average Nernst-boundary-layer thickness was less than 10^{-4} cm and probably greater than 10^{-5} cm. A boundary layer thickness of 10^{-4} cm would result in a concentration difference across the boundary layer of about 3×10^{-2} N at 750 mA/cm^2. This concentration difference

is about 30% of the bulk concentration (0.1 N). However, no variation in either the "membrane" voltage or the radiotracer fluxes was observed when the motor speeds were changed from six to twenty Hertz. This suggests that boundary layers are not a significant resistance in these experiments, and that 10^{-4} cm represents a rather inexact upper limit of the Nernst-boundary-layer thickness.

The remainder of the errors associated with this work appear to be random, statistical errors. Attempts have been made to quantify these statistical errors throughout this work. The estimates of errors have been based primarily on the standard deviations of the experimental quantities. Table 12 lists the approximate standard deviations of various experimental and calculated variables as a percentage of the mean. Table 12 applies only to the radiotracer experiments. The errors associated with the results of Hittorf experiments, Table 1, were generally greater than those for radiotracer experiments. Generally the errors in $\hat{t}_+$ based on the Hittorf experiments resulted from the classic problem of a small difference between large numbers (see Eq. 29). The errors obtained with specific results will be discussed below, individually.

The transference number of sodium ions in Nafion have been determined by both the Hittorf (titration) and radiotracer methods. Fig. 7 shows the radiotracer results as a function of current density. The error bars were calculated from the estimated errors listed in Table 12. The average $\hat{t}_+$ is 0.991 $\pm$ 0.060. This calculated standard deviation is about 6% and corresponds fairly well with the 3.5% to 5.5% error bars. However, a least squares straight line passing through these data has a slope of -1.68×10^{-4} cm^2/mA and a standard deviation of 35%. A statistical t test was performed which showed that the slope was significantly different from zero at the 90% confidence level. This suggests that the transference number may decrease slowly with current density over the range studied, but other results cast doubt on this conclusion. When the t test was applied to the transference-number intercept at zero current density, it showed the transference number to be significantly greater than one, again at the 90% confidence level. These results suggest that the transference number may be a weak function of the current density, but additional data will be needed to clarify this point.

Table 12

Error Estimates for Radiotracer Experiments

Variable	Tracer	Error (%)
C_{*1}	Na^{22}	3
C_{*1}	H^3	2.5
C_{*2}	Na^{22}	1
C_{*2}	H^3	3
Total Tracer	Na^{22}	2.5
Total Tracer	H^3	2
Chamber Volume		0.5
N_*^o	Na^{22}	1
N_*^o	H^3	2
N_*^i	Na^{22}	0.5
N_*^i	H^3	2.5

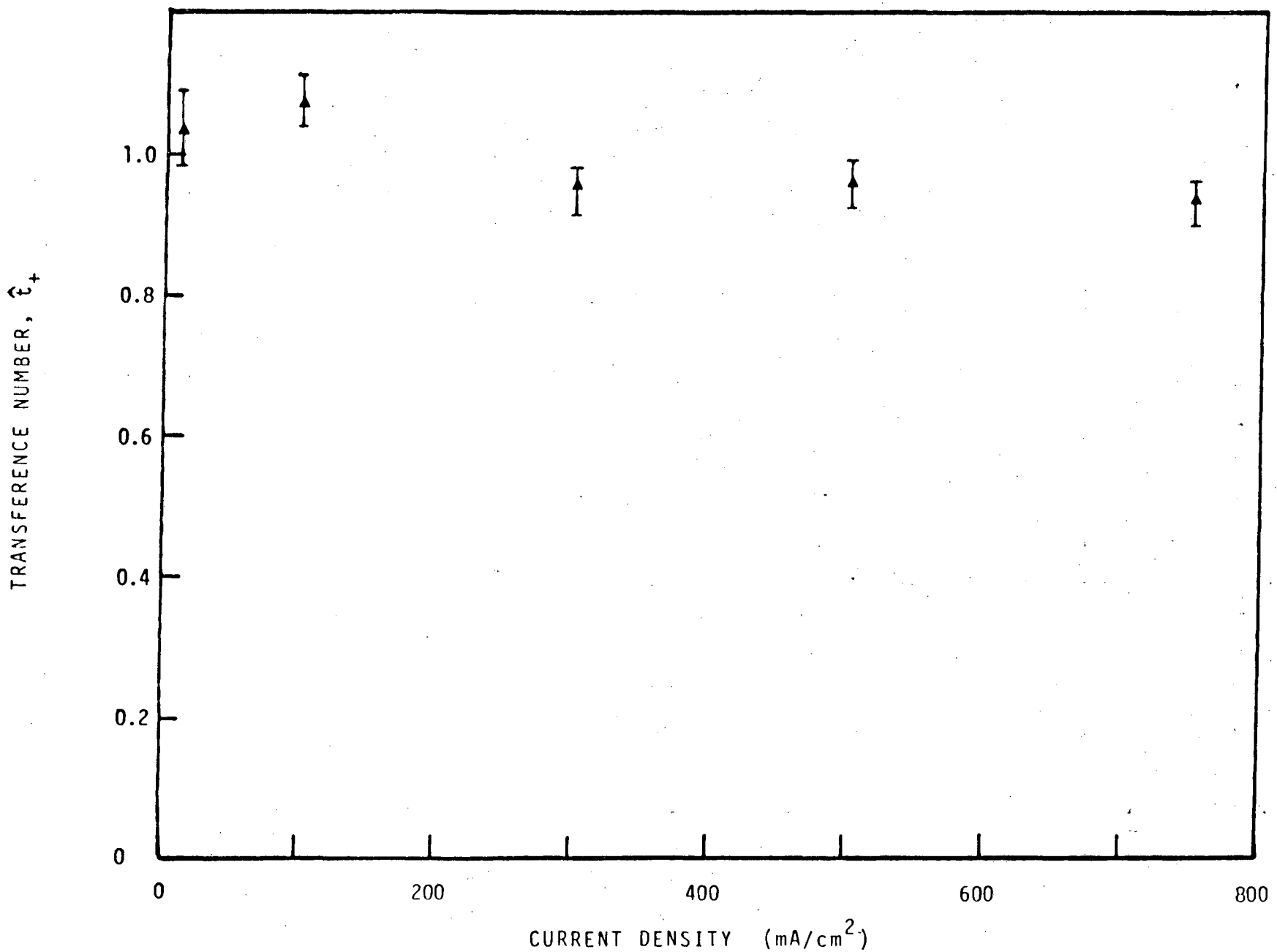

Fig. 7. Sodium-ion transference numbers obtained by radiotracer experiments. Nafion membrane in 0.1 N NaCl solution, at 27°C.

The sodium ion transference number was also obtained by determining the changes in chloride ion concentration in the solutions on each side of the Nafion membrane. Table 4 shows how the individual experiments are subject to considerable variability. If it is assumed that the transference number is independent of current density an average transference number can be calculated ($\hat{t}_+ = 0.971 \pm 17\%$).

These results indicate that the radiotracer method is somewhat more accurate than the Hittorf method, and that the sodium ion transference number is about 0.99. Pintauro performed a series of Hittorf experiments with Nafion membranes in different NaCl solutions having concentrations greater than 1 N. An extrapolation of his data to 0.1 N concentration yields a transference number $\hat{t}_+ = 0.96$. Pintauro did not state his error estimate, but his data suggest a standard deviation of about 5%. His experiments were conducted at a current density of 6.2 mA/cm^2.

Pintauro's results show an improved accuracy over the Hittorf results obtained here and improvements in the technique can undoubtably further reduce the statistical errors, but the Hittorf method will always suffer from the problem of requiring a small difference between large numbers. The radiotracer method, on the other hand, involves the ratio of two fluxes, Eq. 28. The tracer method does involve non-linear equations, and when the flux ratio N_*^i/N_*^o is small, small errors in the ratio produce large errors in the quantity $\alpha\delta$ and also in $\hat{t}_+$. Thus, at low current densities where N_*^i/N_*^o is not much larger than one, the radiotracer method appears to have no inherent advantage over the Hittorf method, but when the flux ratio is larger than about five, the radiotracer method is preferred.

Self-permeability coefficients have been obtained from these experiments. The self-permeability coefficients for sodium ions are listed in Table 7. The average $P_* = 2.05 \times 10^{-5}$ cm^2/s and the standard deviation is $\sigma = 7\%$. This is somewhat larger than the expected standard deviation, calculated from the data in Table 12, of about 4%. This fact may indicate that a source of error is present which has not been adequately accounted for in the calculation of P_*. One obvious possibility for error is temperature variation, but the values of $\ln(P_*)$ are uncorrelated with 1/T, calculated from the average temperatures listed in Table 1.

It is interesting to note that there appears to be a statistically significant correlation between the values of the sodium self-permeability coefficient, P_* and $\hat{t}_+$. This is especially interesting in view of the fact that N_*^i becomes independent of P_* for $\alpha\delta$ less than approximately -5. Thus all but one value of $\hat{t}_+$ listed in Table 7 can be calculated independently, without knowledge of P_*. The only variable which enters into both the determination of $\hat{t}_+$ and P_* is C_{*1}, but the fluctuations in C_{*1} (Table 12) are not large enough to explain the observed variation in either P_* or $\hat{t}_+$. At this time an explanation of the apparent correlation between P_* and $\hat{t}_+$ cannot be given.

It is also interesting to compare the values of P_* to those reported by others. Table 13 shows that the average diffusivity obtained in this work is about 20% greater than that predicted by correcting published data obtained with 1200 equivalent weight Nafion. This degree of agreement is reasonable in view of the circumstances.

The tritium radiotracer experiments were conducted to determine the transport number of water in Nafion membranes. The results are shown in Table 10 and Fig. 8. The error bars shown in the figure represent an estimated standard error (5% - 9%) calculated from the data in Table 12. We are unaware of any comparable radiotracer data in the literature. Figure 8 shows that the observed variations in transport number are greater than the expected statistical fluctuation. This suggests that the water transport number is a function of current density as shown in the figure. However, these data represent a lower transport number than Pintauro found in concentrated sodium chloride solution at a current density of 6.2 mA/cm^2. An extrapolation of Pintauro's data indicate that the water transport number is about 12.5 mole/eq. in 0.1 N NaCl solution. This value is more than twice the value obtained here at a comparable current density. We are unable to throughly explain this descrepancy between our work and Pintauro's results. The same original sheet of Nafion was used in both studies. Approximately three years elapsed between the two studies, and the experimental techniques were different. Pintauro's method involved determination of the volume flow across the membrane. Volume flow was monitored in this work, but it was of the same magnitude as the radiotracer sample volume. This is the result of the small ratio of membrane area to cell volume, and consequently the volume-flow measurements were subject

Table 13

Self-Diffusivities of Sodium in Nafion at 27°C

$D_* \times 10^7$ (cm^2/s)	External NaCl Concentration (M)	Nafion EW (g/eq.)	Reference
10.2	0.05	1200	20
12.1	0.05	1200	21
10.6	0.05	1200	21
12.7†	0.10	1200	22
18.9	0.10	1100	This work
15.7	0.05	1100††	20 - 22

†Expanded membrane, see reference

††Average of the results for 1200 EW membranes corrected to 1100 EW

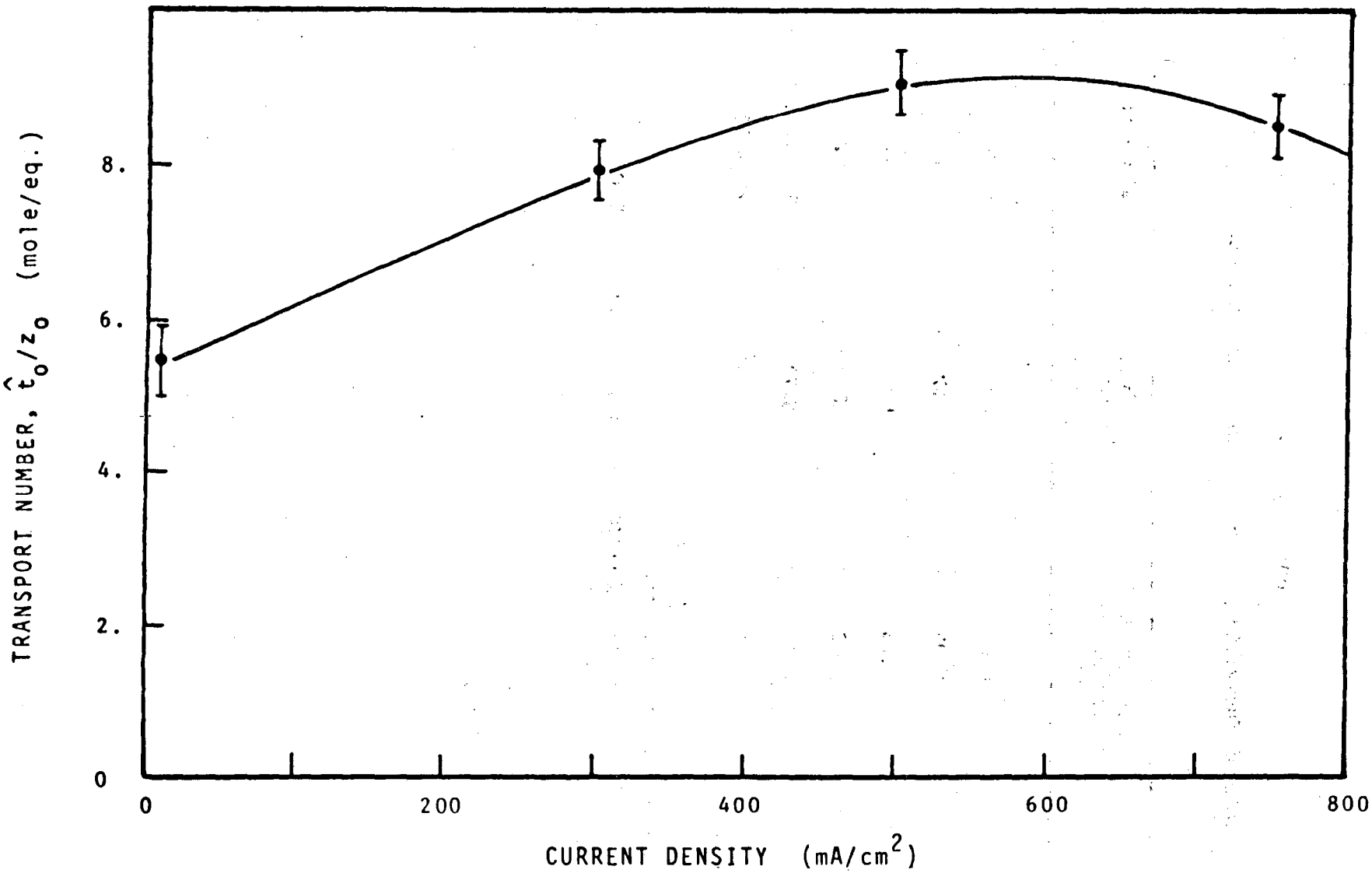

Fig. 8. Water transport number results obtained with radiotracers. Nafion membrane in 0.1 N NaCl solution, at 27°C.

to large percentage errors. Therefore no direct comparison can be made between Pintauro's results and those obtained in this work.

Permeability coefficients for water are shown in Table 10. The average permeability coefficient is $P_* = 2.45 \times 10^{-6}$ cm^2/s, and the standard deviation is about 4%. This standard deviation is in good agreement with the value of 4.5% estimated from the data in Table 12. There are no directly-comparable self-diffusion results for tritium-labled water in the literature, but Yeager and Steck (21) have published a value of self-diffusivity obtained with 1200 equivalent weight Nafion. Their self-diffusivity, corrected to 27°C, is $D_* = 2.81 \times 10^{-6}$ cm^2/s. The self-permeabilities in Table 4 can be converted to self-diffusivities by dividing by the dimensionless solubility, S, of water in Nafion. A value of S = 0.295 was used to obtain an average diffusivity of 8.32×10^{-6} cm^2/s obtained here with 1100 equivalent weight Nafion. These two values of the self-diffusivity are in reasonable agreement considering the difference in equivalent weight.

The pH results shown in Table 11 indicate that hydrogen and hydroxide ions are only minor species in this work. The catholyte showed a slight increase in pH, particularly when the porous silver working electrode was used, but in no case was the amount of hydroxide produced a significant fraction of the charge passed. The hydroxide produced correlated roughly with the small bubble volume observed at the termination of experiments, and appeared to be formed by an electrode reaction at the cathode rather than by a water-splitting mechanism at the membrane.

We conclude from these results that the radiotracer method of determining transport numbers is viable. In general the radiotracer method appears to be somewhat more accurate than the Hittorf method, and the accuracy of both techniques can be improved over the results presented here. Improvements can be made in the Hittorf technique by optimizing the chloride titration method, or by using another analytical technique. The radiotracer results can be improved by increasing the quantity of tracer used and by improved and more frequent sampling. The results indicate that the sodium ion transport number is relatively constant over a large range of current densities when boundary layers are absent. The water transport number on the other hand passes through a maximum as current density increases. It would be interesting

to investigate the effects of temperature and sodium chloride concentration on the water transport number.

CONCLUSIONS

The following conclusions are based on experiments performed with Nafion 7-1100 membranes immersed in 0.1 N NaCl solution at approximately 27°C.

1. The radiotracer method is a viable technique for determining membrane transport numbers.

2. The radiotracer method can be used to simultaneously obtain several transport numbers in a single experiment.

3. Sodium ion transference numbers are not strongly affected by current density, up to 750 mA/cm^2.

4. Water transport numbers do depend on current density in the range 10 mA/cm^2 < i_p < 750 mA/cm^2.

ACKNOWLEDGMENT

The authors wish to thank Professor D. N. Bennion for his assistance and encouragement. This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4511710.

NOMENCLATURE

A = membrane area, cm^2

C_i = concentration of species i in the membrane, $mole/cm^3$

ΔC = total change in salt concentration, $\Delta C_2 - \Delta C_1$, $mole/cm^3$

F_* = average radiotracer flux, $Ci/cm^2 \cdot s$

F = Faraday constant, 96,500 C/eq

i = current density, A/cm^2

L_{ij} = phenomenological coefficient for the transported species i subject to the electrochemical potential gradient of species j, $cm^5/J \cdot s$

N_i = flux of species i, $mole/cm^2 \cdot s$

N^o = flux of radiotracer with zero current, $mole/cm^2 \cdot s$

N^i = flux of radiotracer with non-zero current, $mole/cm^2 \cdot s$

n = total radiotracer in both chambers, Ci

R = gas constant, 8.311 $J/mole \cdot {}^\circ C$

T = absolute temperature, $^\circ K$

t_i = transference number of species i, dimensionless

$\hat{t}_i$ = transference number of chemical i, dimensionless

V = chamber volume, cm^3

$\overline{V}$ = average chamber volume, $(V_1 + V_2)/2$, cm^3

z_i = signed charge of the species, i, eq/mole

α = a constant, see Eq. 24, cm^{-1}

β = a constant, $-N_*/D_*$, $mole/cm^4$

∇ = del operator, cm^{-1}

δ = membrane thickness, cm

ε = reciprocal time constant for migration, Eq. 35, s^{-1}

κ = membrane conductivity, $\Omega^{-1}cm^{-1}$

γ = reciprocal time constant for tracer diffusion, Eq. 30, s^{-1}

ϕ = electric potential, V

μ_i = electrochemical potential of species i, J/mole

Subscripts

ave = average value

E = electrodialysis period

i = species identification index

m = membrane

SD = self-diffusion period

t = value at time, t

1 = on side 1 of the membrane

2 = on side 2 of the membrane

Superscripts

i = the electrodialysis period

o = the self-diffusion period

REFERENCES

1. P. Meares and A. H. Sutton, J. Colloid Interface Sci., 28, 118 (1968).
2. Sixth Quarterly Report, P.O. 4511710, April 1 - June 30, 1982.
3. Seventh Quarterly Report, P.O. 4511710, June 30 - September 30, 1982.
4. Eighth Quarterly Report, P.O. 4511710, October 1 - December 31, 1982.
5. Ninth Quarterly Report, P.O. 4511710, January 1 - March 31, 1983
6. E. Forland, Acta Chemica Scandinavica A, 30, 825-28 (1976).
7. T. R. E. Kressman and F. L. Tye, Discussions of the Faraday Soc., 21, 185-92 (1956).
8. C. Bourdillon, M. Metayer, and E. Selegny, Journal de Chimie Physique, 71 (5), 788-794 (1974).
9. N. Lakshminarayanaiah and V. Subrahmanyan, Journal of Polymer Science, A, 2, 4491-4502 (1964).
10. N. Lakshminarayanaiah, "Transport Phenomena in Membranes," Sect. 5.4, Academic Press, London, 1969.
11. C. Bourdillon, M. Demarty and E. Selegny, Journal de Chimie Physique, 71 (6), 819-27 (1974).
13. C. Ripoll, M. Demarty and E. Selegny, Journal de Chimie Physique, 71 (6), 828-35 (1974).
14. J. S. Newman, "Electrochemical Systems," Ch. 12, Prentice-Hall, New Jersey, 1973.
15. A. H. Sutton, "Transport Processes in a Cation-Exchange Membrane," PhD dissertation, Chemistry Department, University of Aberdeen, Scotland, 1964.
16. D. G. Miller, J. Phys. Chem., 70 (8), 2639 (1966).
17. D. G. Miller, J. Phys. Chem., 71 (3), 616 (1967).
18. F. Helfferich, "Ion Exchange," pp 258-9, McGraw-Hill, New York, 1962.
19. P. N. Pintauro, "Mass Transfer of Electrolytes in Membranes," PhD dissertation, UCLA, Los Angeles, CA, 1980.
20. H. L. Yeager and B. Kipling, The Journal of Physical Chemistry, 83 (14), 1836-39 (1979).
21. H. L. Yeager and A. Steck, J. Electrochem. Soc., 128 (9), 1880-84 (1981).
22. H. L. Yeager, Z. Twardowski and L. M. Clarke, J. Electrochem. Soc., 129 (2), 324-27 (1982).

Appendix A

Pressure History of the Experiments

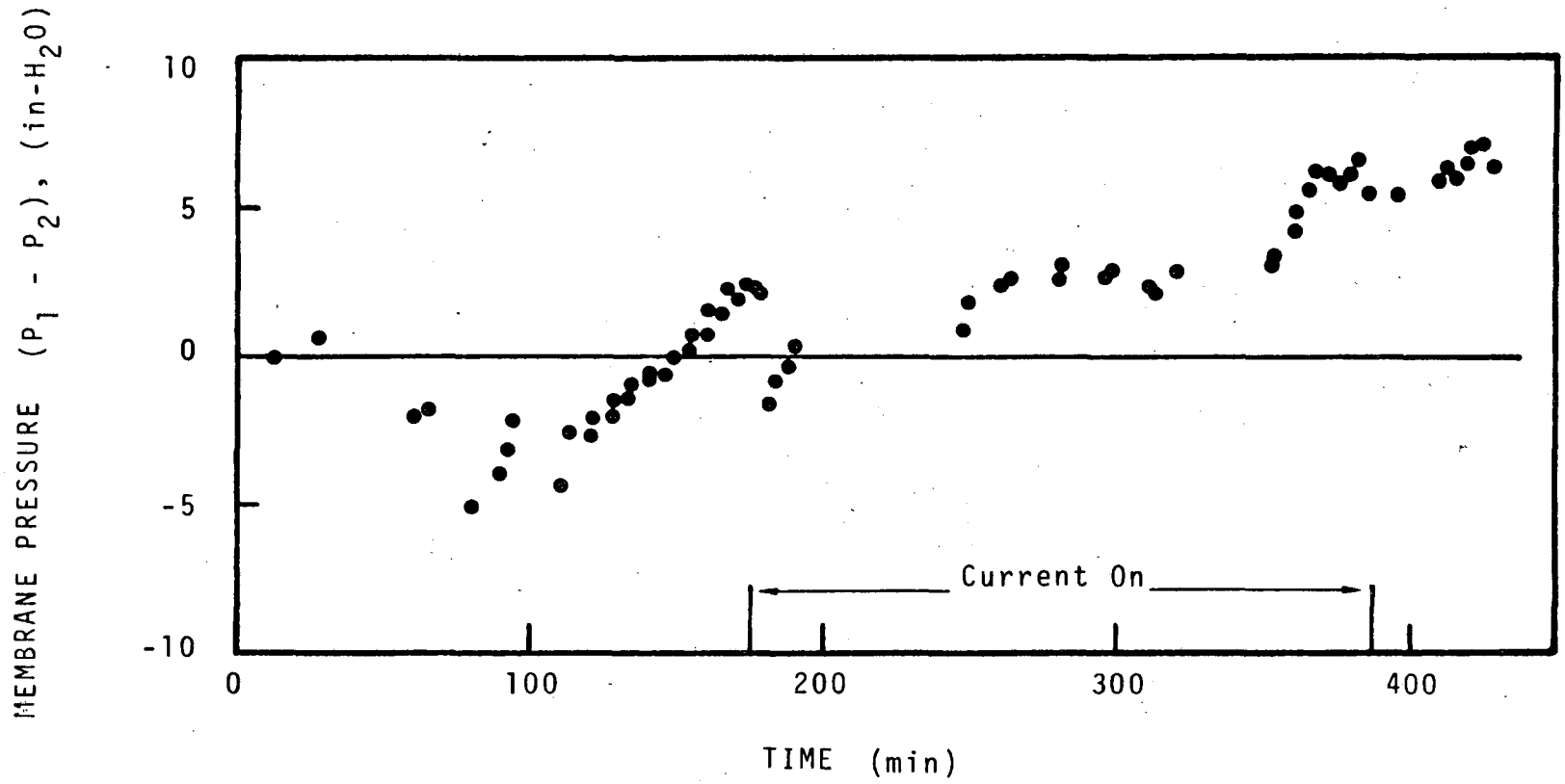

Fig. A1. Pressure difference across a Nafion 7-1100 membrane. Current density = 10 mA/cm^2.

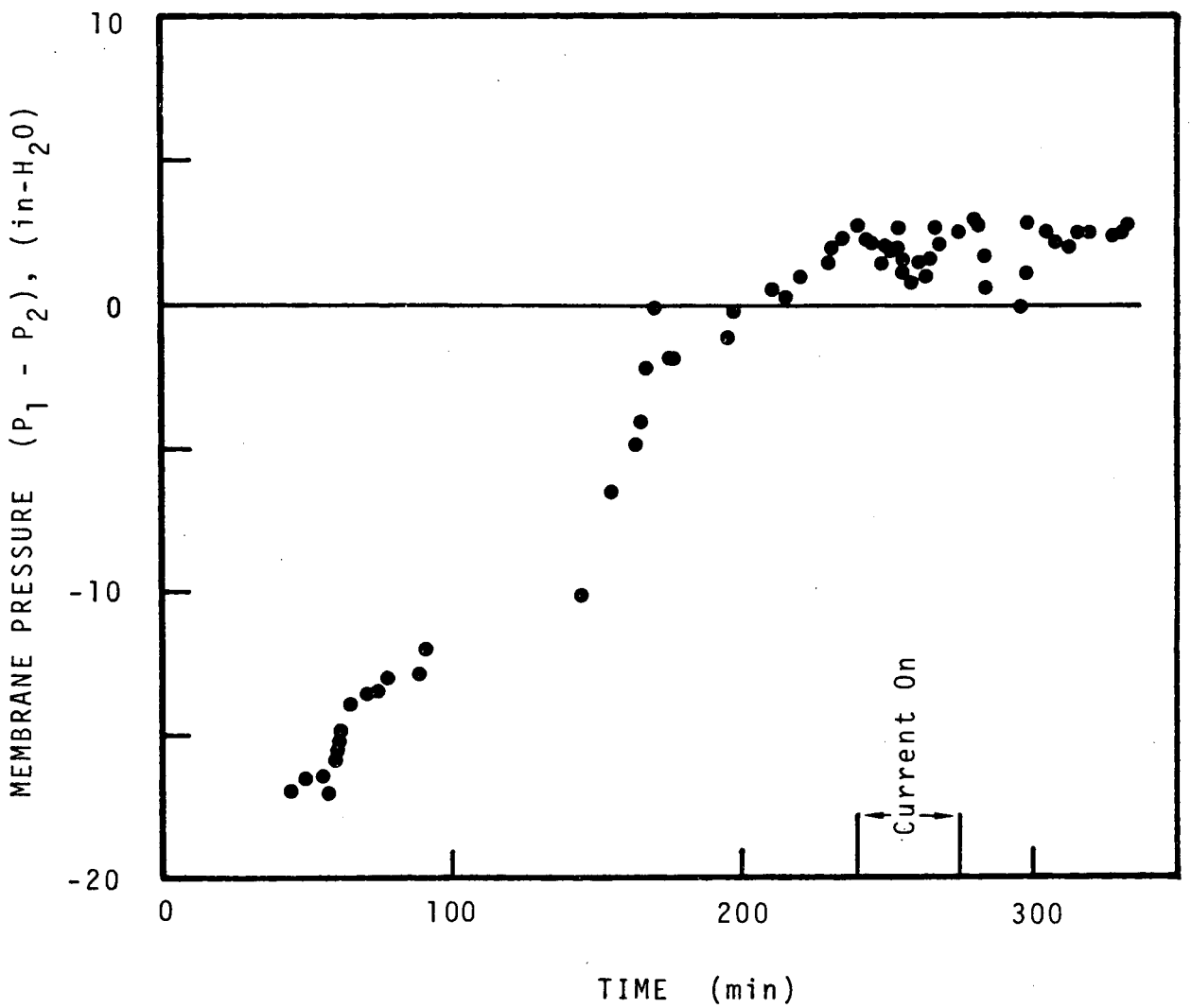

Fig. A2. Pressure difference across a Nafion 7-1100 membrane. Current density = 100 mA/cm^2.

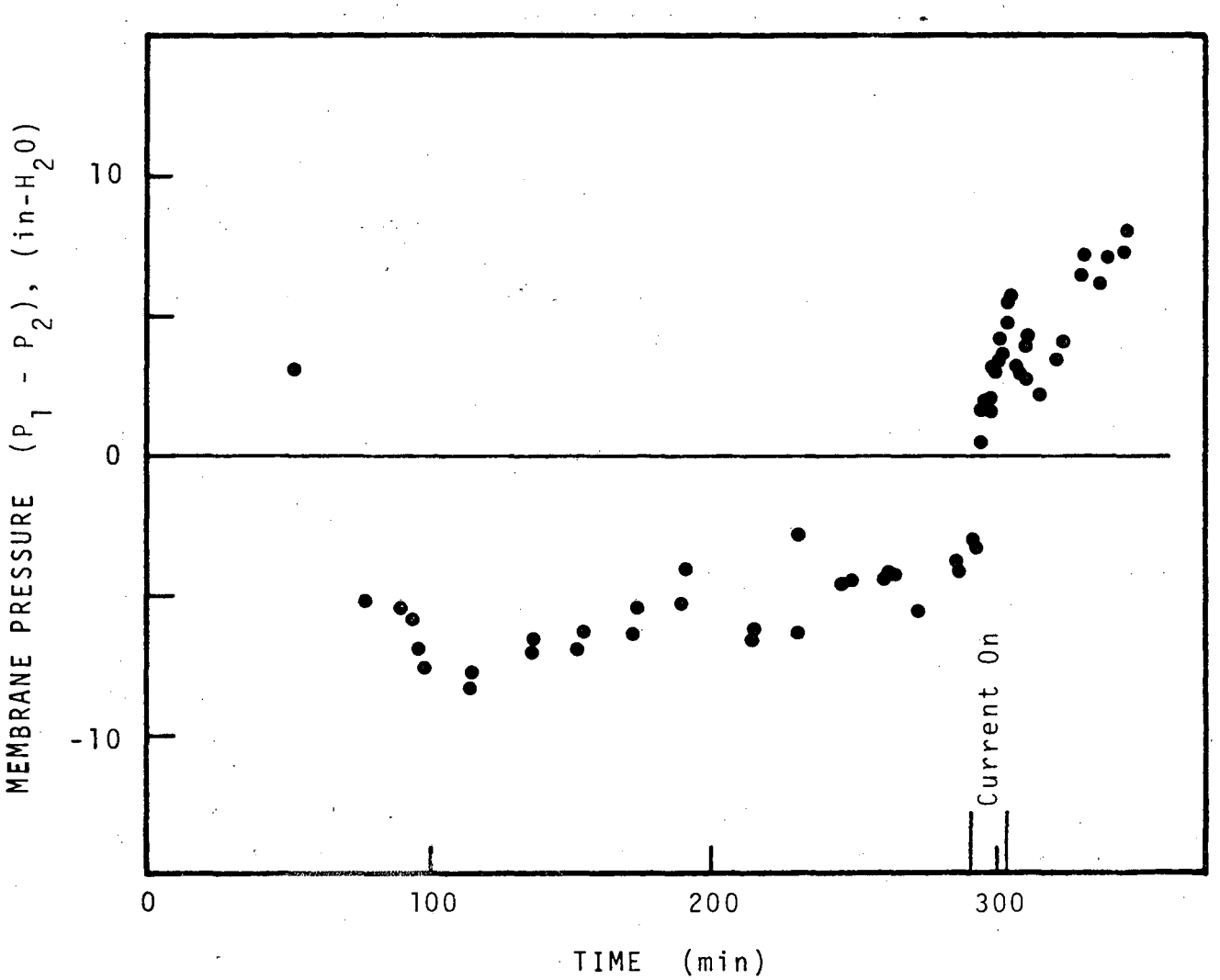

Fig. A3. Pressure difference across a Nafion 7-1100 membrane. Current density = 300 mA/cm^2.

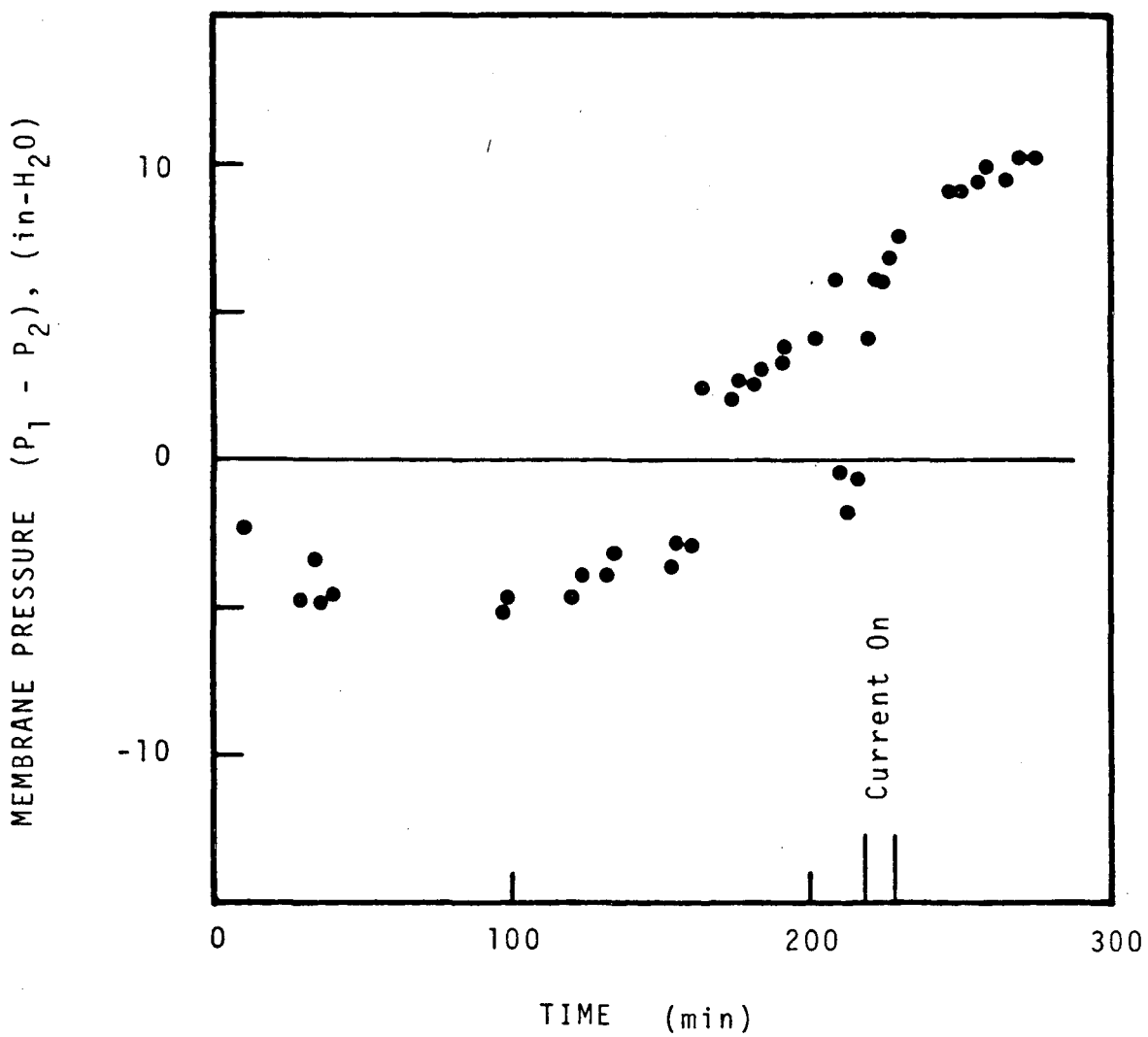

Fig. A4. Pressure difference across a Nafion 7-1100 membrane. Current density = 500 mA/cm^2.

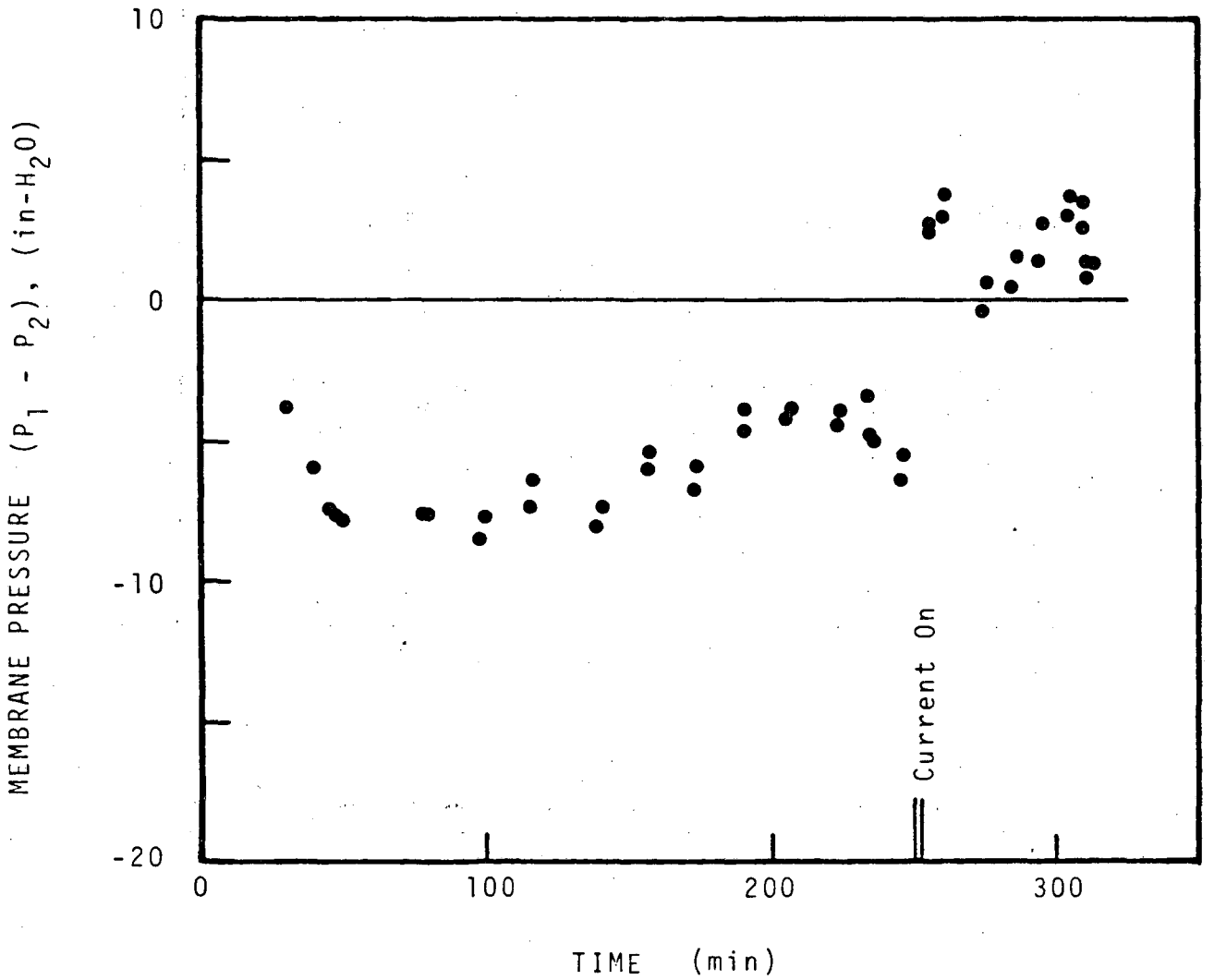

Fig. A5. Pressure difference across a Nafion 7-1100 membrane. Current density = 750 mA/cm^2.

Appendix B

Quarterly Reports

P.O. 4511710

April 1, 1982 through March 31, 1983

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

R. T. Ruggeri

T. R. Beck (Principal Investigator)

Electrochemical Technology Corp.

3939 Leary Way N. W.

Seattle, Washington 98107

Sixth Quarterly Report

April 1 - June 30, 1982

LBL Purchase Order 4511710

In the period from March 31 to June 30, 1982, work was concentrated on two subjects. First, the solubility of sodium ions in Nafion 7-1100 membranes, which were immersed in 0.13 N NaCl at 20. ± 2. °C, was determined, using a radiotracer technique. The sodium ion concentrations were 0.936×10^{-3} and 0.915×10^{-3} (g-mole Na/g-dry-Nafion). The chloride ion solubility was reported last quarter (1). The ion-exchange capacity (IEC) was calculated as the difference between the solubilities of sodium and chloride ions

$$\text{IEC} = 0.920 \times 10^{-3} \text{ g-mole/g-dry-Nafion} \qquad (1)$$

This compares to the value of 0.909×10^{-3} g-mole/g-dry-Nafion specified by DuPont, and Pintauro's (2) result of 0.854×10^{-3} g-mole/g-dry-Nafion. Pintauro's experimental procedure and conditions were slightly different than those employed here. He exchanged hydrogen ions at 25°C, whereas we exchanged sodium ions at 20°C.

The second subject of concern this quarter was the construction of a high-current-density Hittorf cell. A cell capable of conducting approximately 0.1 A/cm^2 was designed and construction is under way. Additional Hittorf experiments using the new cell are planned next quarter.

REFERENCES

1. Fifth Quarterly Report, P.O. 4511710, January 1 - March 31, 1982.

2. P. N. Pintauro, "Mass Transfer of Electrolytes in Membranes," Ph. D. Dissertation, University of California, Los Angeles (1980).

LBL Purchase Order 4511710

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

Seventh Quarterly Report for the Period

June 30, 1982 to September 30, 1982

Prepared for:

LAWRENCE BERKELEY LABORATORY

UNIVERSITY OF CALIFORNIA

One Cyclotron Road

Berkeley, California 94720

By: R. T. Ruggeri

T. R. Beck, Principal Investigator

ELECTROCHEMICAL TECHNOLOGY CORP.
3935 Leary Way N. W.
Seattle, Washington 98107
(206) 632-5965

October, 1982

In the period from June 30 to September 30, 1982, the objectives of this work have been reevaluated while awaiting completion of the high-current-density Hittorf cell. Additional ion solubility experiments have also been completed.

To date, three Hittorf experiments have been completed on two Nafion specimens (1). These experiments were conducted in such a way that the radiotracer flux should have increased when current was passed. In the first experiment the flux of chloride-36 decreased when current was applied. In the second experiment, the chloride-36 flux increased marginally, but the reliability of the calculated increase was not high. In the third experiment, sodium-22 was the tracer and the flux increased when current was applied, but the calculated transference number for sodium was 0.5. These results are indeed curious and might indicate some fundamental error in either the experimental technique or the interpretation of the data. These possibilities have been reviewed and it has been concluded that the possibilities for such errors are both limited and unlikely. One possible source of experimental error is that an ion, or ions, other than Na^+ and Cl^-, is present. The source of additional ions could be "membrane polarization" or "water splitting" which occurs when the salt concentration becomes depleted in the boundary layer adjacent to the membrane. When water splitting takes place, the catholyte becomes acidic and the anolyte basic. No pH measurements were made in the Hittorf experiments, but separate experiments in which pH indicators were used showed pH changes consistent with the water splitting mechanism when the anolyte was unstirred. No pH changes were observed when the anolyte was stirred. The limiting-current experiments reported in the Fifth Quarterly Report also support the conclusion

that water splitting only takes place when the solutions are not being stirred, and thus it is unlikely that water splitting occurred in the well-stirred Hittorf cells.

A second possible source of hydrogen or hydroxyl ions could be chemical reaction at the working electrodes. Porous silver electrodes were used in all Hittorf experiments, and the maximum current density was 10 mA/cm^2. From analogy with battery electrodes it was assumed that only chloride ions would be produced or consumed at the electrodes, but this assumption was not verified.

Another possible source of hydrogen ions is the Nafion membrane itself. Prior to performing the Hittorf experiments the Nafion specimens were boiled in water and soaked in sodium chloride solution. Preliminary calculations indicated that the Nafion could be converted from the acid form to the sodium form in a few hours. Subsequent ion-exchange-capacity experiments have shown that about 5% of the Nafion sites were in the H^+ form for the first two Hittorf experiments. The Nafion specimen used for the third Hittorf experiment was completely converted to the sodium form.

As the preceeding discussion indicates, there are several possible sources of either hydrogen or hydroxyl ions in the three Hittorf experiments conducted thus far, but none of these sources appears to be sufficient to explain the observed anomalies in the radiotracer fluxes which occur when a current is passed. This evidence therefore supports the conclusion that either a calculational error or an incorrect assumption has been made while processing or interpreting the data. After reviewing the entire data reduction process, one assumption has emerged as most suspect: the transference numbers are independent of current density. A preliminary literature search

was conducted on this subject and no discussion of a direct influence of current density on transference numbers was found. The only effect of current density is indirect, resulting from concentration changes within boundary layers adjacent to the membrane. It should be pointed out, however, that only a very few references have dealt with this subject in recent years, and no data were obtained for Nafion membranes in sodium chloride solution. In view of this situation, it has been decided to shift the primary emphasis of this work from an investigation of the cross-coefficients resulting from the addition of radiotracers in Hittorf experiments to an investigation of the effects of current density on transference numbers.

Another factor which was considered when making the decision to change the primary thrust of this work was the precision of the results obtained thus far in Hittorf experiments. The standard deviations of the parameters calculated from Hittorf experiments varied from about 1% up to 50%, depending upon the parameter involved and the method of obtaining its value. This precision is considered adequate for many purposes, but is probably insufficient to reliably determine the radiotracer cross-coefficients. Meares et al. (2,3) have reported the results of a similar investigation of a different type of ion-exchange membrane. Meares reported standard deviations on the order of only a few percent, but was unable to unambiguously determine the sought cross-coefficients. In view of this situation, it was concluded that the most productive use of the available resources would be to undertake an investigation, using radiotracers, of the effects of current density on transference numbers. In addition to providing answers to the questions raised by the three Hittorf experiments which have been completed, the results of this proposed work will provide data over a wide range of current

densities which can be used in the mathematical model being developed at Brigham Young University by Professor Bennion.

The ion solubility experiments have been discussed in previous reports (1,4). The results of all experiments are summarized in Table 1.

REFERENCES

1. Fifth Quarterly Report, P.O. 4511710, January 1 - March 31, 1982.

2. P. Meares, T. Foley and J. I. Menqual, "Membrane Transport Processes," Vol. 1, p. 1, J. F. Hoffman, Ed., Raven Press, New York, 1978.

3. P. Meares, "Echanges Ioniques Transmembranaires Chez Les Vegataux," Editions du Centre National de la Recherche Scientifique, No. 258, M. Thellier, A. Monnier, M. Demarty and J. Dainty, Eds., Paris, France, 1977.

4. Sixth Quarterly Report, P.O. 4511710, April 1 - June 30, 1982.

TABLE 1

Ion Solubility in Nafion Specimens

Immersed in 0.13 N NaCl at 20 ± 2°C.

Tracer Ion	Cl^-	Na^+
Concentration in Membrane (mol/g dry mem.)	4.60×10^{-6}	9.36×10^{-4}
	6.24×10^{-6}	9.15×10^{-4}
		8.74×10^{-4}
		8.92×10^{-4}
Average	5.42×10^{-6}	9.04×10^{-4}
Standard Deviation	15%	3%

LBL Purchase Order 4511710

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

Eighth Quarterly Report for the Period

October 1, 1982 to December 31, 1982

Prepared for:

LAWRENCE BERKELEY LABORATORY

UNIVERSITY OF CALIFORNIA

One Cyclotron Road

Berkeley, California 94720

By: R. T. Ruggeri

T. R. Beck, Principal Investigator

ELECTROCHEMICAL TECHNOLOGY CORP.

3935 Leary Way N. W.

Seattle, Washington 98107

(206) 632-5965

January, 1983

During the past quarter, ending December 31, 1982, additional ion-solubility data have been obtained for Nafion 7-1100 specimens immersed in NaCl solution. Table 1 compares the results of radiotracer experiments with calculated values extrapolated from Pintauro's (1) work. All results shown in Table 1 are based on experiments using Nafion samples originally cut from a single large sheet. At least two years have now passed since Pintauro's experiments were completed. Table 1 shows that the "apparent" fixed ion concentration (χ), determined as ($C_+ - C_-$), depends slightly on the salt concentration in the external solution. Du Pont lists the fixed ion content of this type of Nafion as 9.09×10^{-4} mol/g dry membrane. Pintauro determined the fixed ion concentration as 8.54×10^{-4} mol/g dry membrane, at a solution concentration of 2 N NaCl. Helfferich (2) has discussed the dependence of the apparent fixed ion concentration on test conditions, and attributes the dependence primarily to competition of different ions for the available fixed-ion sites. The data in Table 1 suggest that two effects are present in these Nafion specimens: χ increases slightly with the external solution concentration, and χ also increases with membrane age.

During the past quarter work has also progressed toward determination of the dependence of transference numbers on current density. The high-current-density Hittorf cell has been constructed and preliminary tests to determine the Nernst diffusion layer thickness have been completed. These tests were conducted by measuring the limiting cathodic current while plating silver on a silver electrode. The results indicate a diffusion layer thickness (δ) of about 1 μm. Boundary layer effects should therefore be small, depending on the solution concentration (C_e), for current

densities less than about 1 A/cm^2. Thus far, the results obtained with the high-current density Hittorf cell are encouraging, and experiments to determine the transference numbers at high current densities are planned as soon as modifications to the cell are completed.

REFERENCES

1. P. N. Pintauro, "Mass Transfer of Electrolytes in Membranes," Ph.D. Dissertation, University of California, Los Angeles (1980).

2. F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York, 1962.

Table 1

Comparison of Equilibrium Data for Nafion 110

in NaCl Solution at 25°C

	Radiotracer**			Pintauro*	
C_e (N)	C_+ (mol/g)	C_- (mol/g)	Fixed Ion Con. (mol/g)	C_+ (mol/g)	C_- (mol/g)
0.02	8.89×10^{-4}	1.38×10^{-6}	8.88×10^{-4}	8.45×10^{-4}	-6.18×10^{-6}
0.13	8.86×10^{-4}	5.4×10^{-6}	8.81×10^{-4}	8.62×10^{-4}	1.02×10^{-5}
1.00	9.98×10^{-4}	7.17×10^{-5}	9.26×10^{-4}	9.91×10^{-4}	1.38×10^{-4}

* Calculated from linear correlations. The data at 0.02 and 0.13 N external solution are extrapolations outside the range of the original data.

** Experiments at 0.02 and 1.0 N concentration were conducted at 25 ± 0.5°C. At 0.13 N concentration the temperature was recorded but not controlled at 20 ± 2°C.

LBL Purchase Order 4511710

DEVELOPMENT OF MULTICOMPONENT TRANSPORT THEORY AND TRANSPORT DATA FOR MEMBRANES IN CONCENTRATED ELECTROLYTES

Ninth Quarterly Report for the Period

January 1, 1983 to March 31, 1983

Prepared for:

LAWRENCE BERKELEY LABORATORY

UNIVERSITY OF CALIFORNIA

One Cyclotron Road

Berkeley, California 94720

By: R. T. Ruggeri

T. R. Beck, Principal Investigator

ELECTROCHEMICAL TECHNOLOGY CORP.
3935 Leary Way N. W.
Seattle, Washington 98107
(206) 632-5965

April, 1983

In the period between January 1 and March 31, 1983, work has continued to investigate the effects of high current density on the selectivity of Nafion 7-1100 membranes immersed in NaCl solution. Testing was performed with the new high-current-density Hittorf cell which showed negligible boundary-layer effects with Nafion membranes in 10^{-2} N NaCl solution up to current densities of over 100 mA/cm^2. Experiments were performed in 10^{-1} N NaCl solution at current densities between 10 mA/cm^2 and 500 mA/cm^2. Radioactive sodium and hydrogen were used as tracers for sodium ions and water. Each experiment actually consisted to two parts. First the self diffusion coefficients of the radiotracers was determined at zero current with equivalent solutions on each side of the membrane. Then a constant current was passed and the new steady-state flux of each radiotracer was obtained. In addition the concentration changes occurring in the two solutions separated by the membrane were determined by specific ion titration of chloride with silver nitrite.

The data have not yet been reduced using computer analysis but some hand calculated results are summarized in Table 1. The radiotracer data provided estimates of both a minimum and a maximum transference number. The minimum t_+ assumes the diffusion flux is independent of the current density and that the increased radiotracer flux results only from migration of ions. The maximum t_+ assumes that the diffusion flux drops to zero when a current flows. As the data in the table show, the minimum and maximum estimates approach a single value as the current density increases. The data also indicate that the ion selectivity of Nafion membranes decreases at current densities above about 100 mA/cm^2.

Table 1

Transference Numbers of a Nafion 7-1100 Membrane in 0.1 N NaCl Solution at 26.5 ± 0.8°C

Exp. #	Current Density (mA/cm^2)	Radiotracer t_+		Hittorf t_+	
		minimum	maximum	t_+	Estimated Standard Error
A	10	0.556	1.274	1.20	0.17
B	100	0.938	1.013	1.11	0.12
C	500	0.855	0.868	0.775	0.23

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720