APPLICATION OF A CATION EXCHANGE MEMBRANE TO A SODIUM ION PUMP

Dear Sir:

Recently, carrier-containing membranes which can pump specific ions from a dilute to a concentrated solution phase have been developed^{4,5)}. Cussler *et al.*¹⁻³⁾ constructed a liquid membrane containing monensin as a mobile carrier. The proton of the carrier was replaced by a sodium ion in an alkaline solution and vice versa in an acid solution. Therefore, the sodium ion could be transferred against its concentration gradient by the counter-current movement of the proton. Shimidzu *et al.*^{6,7)} reported that poly (3-vinyl-1, 4-butyrolactone-co-acrylonitrile) membrane exhibits a similar function using lactone as a fixed carrier.

In both types of membrane, the transport of each sodium ion is achieved at the cost of only one proton diffusing in the opposite direction. Consequently, these membranes function as cation exchange membranes, although they have selectivity for specific ions. The leakage of acid limits the amount of sodium ion which can be moved¹⁾. Hence, one may define the pump efficiency of the membrane as the ratio of the amount of pumped sodium ion to that of migrated proton.

The usual cation exchange membranes have not been applied to such an ion pump. The purpose of this letter is to show the pump efficiency of commercially available cation exchange membrane.

Experimental apparatus and procedures

The membrane used was Selemion CMV manufactured by Asahi Glass Co., Ltd.

The diffusion cell was composed of a pair of cylindrical half-cells (56 cm³) and the membrane holder was sandwiched between them. The cross-sectional area of the membrane was 8.55 cm². The membrane, immersed in 3-M NaNO₃ aqueous solution, was set in the holder. Then, each half-cell was filled with aqueous solutions 1 and 2, respectively, the compositions

of which are shown in **Table 1**. Both solutions were stirred and kept at 25±1°C. The concentration of proton in solution 1, $C_{H^+}^1$, and that of sodium ion in solution 2, $C_{Na^+}^2$, were measured by a pH meter and a sodium ion meter, respectively.

Results and discussion

i) The case with chemical reaction **Figure 1** shows the time concentration history for $C_{H^+}^1$ and $C_{Na^+}^2$, when 0.1-M NaNO₃ and 0.1-M HNO₃ solution (solution 1) and 0.1-M NaOH (solution 2) were fed into each cell. Hence, the proton diffused from solution 1 to 2 and reacted with hydroxide ion, while the sodium ion moved from solution 2 to 1 against its concentration gradient. The coincidence of these two curves in Fig. 1 shows that equimolar amounts of sodium ion and proton were exchanged. This was in accord with the observed result that the movement of nitric ion was negligible.

The average flux of sodium ions from 0 to 60 min calculated from Fig. 1 was compared with those observed by Cussler *et al.*¹⁾ and Shimidzu *et al.*⁹⁾ as shown in Table 1. It was found that the flux observed in this study was very high.

After 15 to 20 hours, the system reached near-equilibrium. The concentration of proton and sodium ion in both solutions as well as the membrane potential at that stage are also listed in Fig. 1. The observed

Fig. 1 Time-concentration history of $C_{H^+}^1$ and $C_{Na^+}^2$

Table 1 Comparison of efficiency of pump and flux

Type of membrane	Solution 1	Solution 2	Efficiency of pump	Flux [mol/cm ² ·s]
Liquid (octanol-monensin) ¹⁾	0.1-M NaCl 0.1-M HCl	0.1-M NaOH	0.67	6.3×10^{-9} (400 min. av.)
Synthesized polymer ⁹⁾	0.85-M NaCl 1.00-M HCl	0.84-M NaOH	—	1.9×10^{-8} (12 h. av.)
A) Cation exchange membrane	0.10-M NaNO ₃ 0.10-M HNO ₃	0.10-M NaOH	0.90	6.2×10^{-8} (60 min. av.)
B) Cation exchange membrane	0.10-M NaNO ₃ 0.10-M HNO ₃	0.10-M NaNO ₃	0.91	1.7×10^{-8} (60 min. av.)

Fig. 2 Time-concentration history of $C_{H^+}^1$

membrane potential is -73.0 mV. This value is nearly equal to -70.6 mV and -76.6 mV, which latter values were calculated by the following Donnan potential equation based on the observed concentration of sodium ion and proton, respectively.

$$E = -\frac{RT}{\mathcal{F}} \ln \frac{C_{Na^+}^1}{C_{Na^+}^2} = -\frac{RT}{\mathcal{F}} \ln \frac{C_{H^+}^1}{C_{H^+}^2}$$

ii) The case without chemical reaction The pump system in Fig. 2 was of a physical nature when 0.1 -M $NaNO_3$ and 0.1 -M HNO_3 solution (solution 1) and 0.1 -M $NaNO_3$ (solution 2) were fed into each cell, respectively. As compared with Fig. 1, the flux in Fig. 2 was low, since the pump was driven only by diffusion of protons without reaction. The membrane potential observed at equilibrium is -17.0 mV, which is close to the -17.1 mV and -18.1 mV calculated by the Donnan potential equation based on the observed Na^+ and H^+ concentrations, respectively.

Pump efficiency As shown in Table 1, the cation exchange membrane was proved to have high efficiency for a sodium ion pump driven by the proton concentration gradient, not only for the case with chemical reaction but also for the case with diffusion alone.

Nomenclature

$C_{Na^+}^i$	= concentration of sodium ion in solution i	[mol]
$C_{H^+}^i$	= concentration of proton in solution i	[mol]
E	= membrane potential	[mV]
$\mathcal{F}$	= Faraday constant	[C]
$\mathcal{R}$	= gas constant	[V · C/K]
T	= temperature	[K]
t	= time	[h]

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