On the Electrolytic Rectification Effect in Ion-exchange Membranes

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The rectification effect has been observed with many biological membranes.1) In these systems, a mechanism based on the strength of the contributions of the ionic conduction has been frequently considered. Recently, Lovreček and his co-workers2) observed the rectification effect in the polyelectrolyte systems. These investigations suggest the possibilty that electric circuits might be constructed with ions as charge carriers. The ions are inferior in their low mobility, but are superior in their various species, to electrons as a charge carrier. This report is our first paper to treat this problem. An experimental and a theoretical treatment of the rectification system of ion-exchange membranes will be given.

Experimental

The ion-exchange membranes used were heterogeneous and were prepared from poly(vinyl chloride) and pulverized ion-exchange resins (commercially-available, Amberlite IR-120 and IRA-400). The membranes were thoroughly washed with hydrogen chloride and sodium hydroxide solutions and then with deionized water. The cation-exchange membrane was made up into the hydrogen form, and the anion-exchange membrane, into the hydroxide form. These membranes were pressed face to face into a double membrane and sandwiched between the two stainless-steel electrodes. Each membrane was 1 cm^2 in area and 0.3 mm. thick. The water content of the membranes, 56% by weight, was maintained through the measurement period by enclosing them in a sealed box.

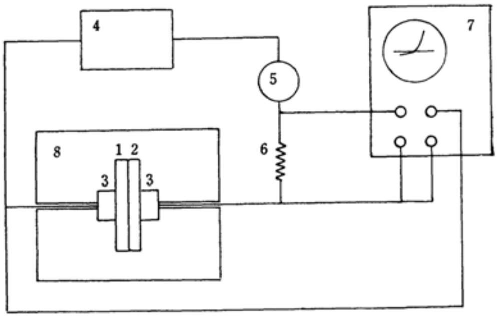

Fig. 1. Apparatus.

1. Cation-selective membrane
3. Anion-selective membrane
3. Electrodes (stainless steel)
4. Voltage source
5. Ammeter
6. Resistance (10 kΩ)
7. Oscilloscope
8. Constant-moisture chamber

The measuring apparatus is shown in Fig. 1. A constant voltage was supplied by a battery, and an alternating voltage, by test-oscillators, Toa-Dempa CR-1E ($10^{-2}\sim10^3$ c. p. s.) and National RC-5A ($25\sim10^5$ c. p. s.). The electric current was measured with a micro-ammeter and an oscilloscope.

Results and Discussion

Constant Voltage - Current Characteristics.— The system in which the positive electrode is connected to the cation-selective membrane and the negative electrode to the anion-selective membrane is highly resistant to the

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1) W. F. Floyd, "Modern Aspects of Electrochemistry," Ed. by J. O'M. Bockris, Butterworths Sci. Publ., London (1954), p. 277.

2) B. Lovreček, A. Despic and J. O'M. Bockris, *J. Phys. Chem.*, **63**, 730 (1960).

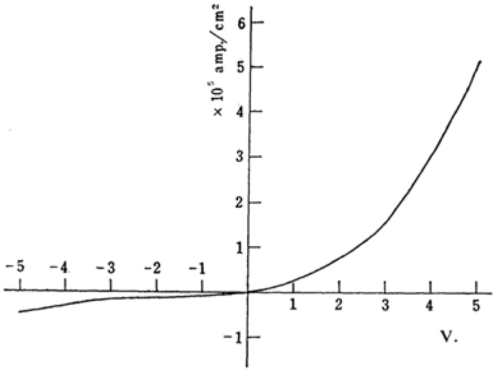

Fig. 2. Current plots versus constant voltages.

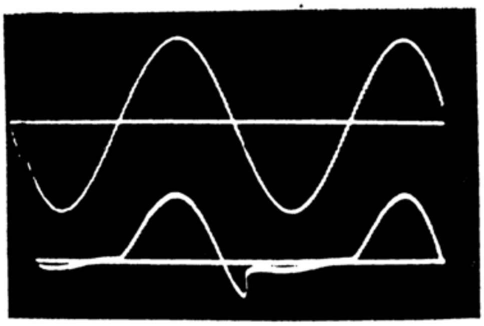

Fig. 3. Rectification of alternating sine-wave current.
Upper curve, input ; Lower curve, output

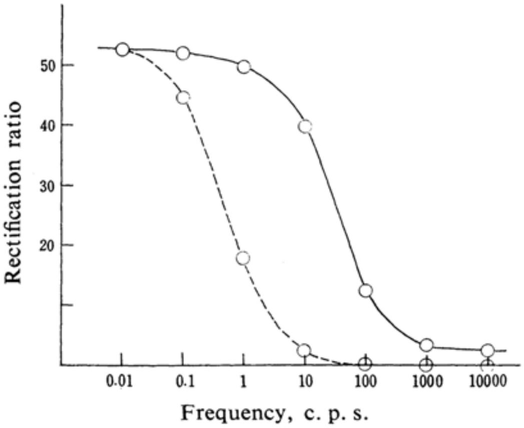

Fig. 4. Dependence of rectification ratio on frequency. (Rectification ratio stands for the current ratio of the forward against the inverse direction.)
Steady line, inverse → forward direction
Dotted line, forward → inverse direction

direct current in comparison with the case where the reverse polarity is applied. The current ratio of the forward direction to the reverse one attains 100 or more. A diagram of the current versus the voltage is shown in Fig. 2. The electric current in the forward direction is stable against the passage of time, while in the reverse direction it has a trend to increase with the lapse of time. The values given in Fig. 2 were read at 30 sec. after the application of a voltage. An increase in the applied volage in the reverse direction results in a gradual increase in the current after an initial trend to saturation.

The relationship between the electric current, i, and the applied voltage, V, is represented by Eq. 1 ;

$$i = i_0 \ (e^{\alpha V} - 1) \qquad (1)$$

where the experimental parameters, i_0 and α, have the following values in the present experiment ;

$$i_0 = 5.0 \times 10^{-1} \text{ amp./cm}^2$$

$$\alpha = 0.49$$

This relation will be discussed in the following section.

Alternating Voltage-Current Characteristics.—The rectification effects are very effective when alternating voltages with very low frequencies (lower than 1 c. p. s.) are applied to the system. An example is shown in Fig. 3. However, it must be pointed out that a clear inflection point appears where the polarity changes from the reverse direction to the forward one, while, when the applied voltage in the forward direction is decreased, no current is observed at a finite value of the applied voltage and then the reversed current becomes to be running. A further decrease in the forward voltage and then an increase in the reverse voltage result in an initial increase in the reverse current, followed by an abrupt decrease, and then the reverse current attains a saturation value. There is observed a hysteresis with a negative resistance in the current-voltage diagram. This is found as a spike current in a current wave. This may be caused by a membrane potential and a capacitance of a liquid film adjacent to the membrane.

When an alternating voltage with frequencies higher than 1 c. p. s. is applied, the rectification effect becomes poorer. One of the observed result is shown in Fig. 4. The primary cause would be a contribution by the capacitance current, based on the capacitance of the membrane system. Assuming an R-C parallel circuit as the simplest equivalent circuit of the system, the following values are measured ; $R = 5 \times 10^3$ ohm and $C = 7 \times 10^{-6}$ F. It is estimated from this that the contribution of the capacitance current is major at frequencies higher than $f = 1/2\pi CR = 4.54$ c. p. s. A contribution of the relaxation effect of the ionic atmosphere[3] will appear at very much higher frequencies, probably 10^7 or higher.

Theoretical Considerations.—The charge carriers in this system will be ions; hydrogen ions (protons) and hydroxide ions in this case. Hydrogen ions are rich in the cation-selective membrane, and hydroxide ions are rich in the anion-selective membrane. The distribution of these carriers is ruled by Boltzmann's law in an equilibrium state. The density, n, of protons is given by:

$$n_x = n_0 \exp(-e\varphi_x/\boldsymbol{k}T) \tag{2}$$

where e the elementary charge, $\boldsymbol{k}$ the Boltzmann constant, and T, the absolute temperatures. The potential, φ, of protons is low in the cation-selective membrane phase (I) and high in the anion-selective membrane phase (II); it is schematicaly shown in Fig. 5.

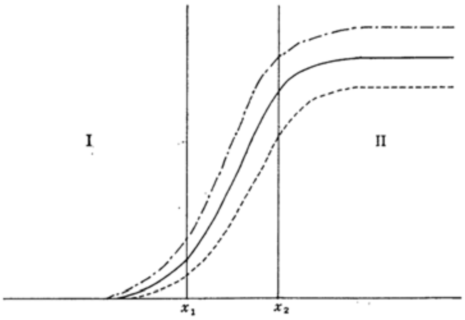

Fig. 5. Potential curve for protons.
I, cation-selective membrane
II, anion-selective membrane
Intermediate, transition region
Steady line, no applied voltage
Dotted line, forward bias voltage
Chain line, inverse bias voltage

The total protonic current is given by adding an driving current to a diffusion current; that is,

$$\begin{aligned} i_x &= eu_n n_x \frac{d\varphi_x}{dx} - eD_n \frac{dn_x}{dx} \\ &= en_x \frac{d\varphi_x}{dx}\left(u_n - \frac{e}{\boldsymbol{k}T}D_n\right) \end{aligned} \tag{3}$$

In the absence of a bias valtage, Einstein's relation holds true between the mobility, u_n, and the diffusion constant, D_n, of protons; that is,

$$u_n = (e/\boldsymbol{k}T)D_n \tag{4}$$

therefore, the total current does not run.

When a forward voltage is applied, the electric potential difference becomes small in the transient region, as is shown by a dotted line in Fig. 5. As a result, a diffusion current surpasses a driving current and protons flow from the transient region into the region II by diffusion. Then the density of protons in the region II becomes

$$n_x = n_{\text{II}} + \Delta n_x \tag{5}$$

according to the principle of electroneutrality, hydroxide ions increase by the same quantity, Δn_x, in this region. At the same time, the excess protons disappear in the formation of water molecules with hydroxide ions. The rate of this recombination reaction, $\boldsymbol{R}$, is:

$$\begin{aligned} R(x) &= rn_x m_x = r(n_{\text{II}} + \Delta n_x)(m_{\text{II}} + \Delta n_x) \\ &= rn_{\text{II}}m_{\text{II}} + rm_{\text{II}}\Delta n_x \\ &= g + (1/\tau_n)\Delta n_x \end{aligned} \tag{6}$$

where m is the density of hydroxide ions, $g = rn_{\text{II}}m_{\text{II}}$ is the rate of the thermal decomposition of water molecules, and $\tau_n = 1/rm_{\text{II}}$ is the mean life-time of protons in the region II.

Under such circumstances, the diffusional flow of protons is expressed by:

$$D_n \frac{dn(x+dx)}{dx} - D_n \frac{dn(x)}{dx} = (R(x) - g)dx \tag{7}$$

or

$$D_n \frac{d^2n}{dx^2} = R(x) - g \tag{8}$$

The boundary condition that, if $x \to \infty$, $n(x)$ equals n_{II}, must be satisfied. The solution of Eq. 8 is at the boundary $x = x_2$:

$$n(x_2) - n_{\text{II}} = C \exp\{-(x - x_2)/L_n\} \tag{9}$$

where $L_n = \sqrt{\tau_n D_n}$ is the mean distance which protons proceed in the region II until their disappearance.

Therefore, the current carried by the protonic diffusion is given by:

$$\begin{aligned} i_n(x_2) &= -eD_n\left(\frac{dn(x)}{dx}\right)_{x=x_2} \\ &= \frac{eD_n}{L_n}\{n(x_2) - n_{\text{II}}\} \end{aligned} \tag{10}$$

From Boltzmann's law,

$$n(x_2) = n_{\text{II}} \exp(eV/\boldsymbol{k}T) \tag{11}$$

These relations lead to the final expression:

$$i_n(x_2) = \frac{eD_n}{L_n} n_{\text{II}}(\exp(eV/\boldsymbol{k}T) - 1) \tag{12}$$

Exactly the same relation holds true for hydroxide ions. Therefore, the total current is expressed by:

$$i = e\left(\frac{D_n n_{\text{II}}}{L_n} - \frac{D_m m_{\text{II}}}{L_m}\right)(\exp(eV/\boldsymbol{k}T) - 1) \tag{13}$$

where the subscript n refers to protons and the subscript m, to hydroxide ions.

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[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Pub. Corp., New York (1950) p. 211.

TABLE I. PARAMETERS OF CHARGE-CARRIERS

	Hydrogen ion	Hydroxide ion
Density in cation-selective membrane, cm^{-3}	$n_{\rm I}=4.17\times10^{17}$	$m_{\rm I}=8.67\times10^{9}$
Density in anion-selective membrane, cm^{-3}	$n_{\rm II}=4.41\times10^{9}$	$m_{\rm II}=8.18\times10^{17}$
Mobility, cm^2/V. sec.	$u_{\rm n}=3.0\times10^{-3}$	$u_{\rm m}=1.7\times10^{-3}$
Diffusion constant, cm^2/sec.	$D_{\rm n}=7.8\times10^{-5}$	$D_{\rm m}=4.4\times10^{-5}$
Mean life-time, sec.	$\tau_{\rm n}=6.6\times10^{-12}$	$\tau_{\rm m}=1.3\times10^{-11}$
Mean invation-distance, cm.	$L_{\rm n}=2.25\times10^{-8}$	$L_{\rm m}=2.4\times10^{-8}$
Thermal generation rate, cm^{-3}/sec.	$g=6.7\times10^{20}$	

When a reverse bias voltage is applied, the density of protons at $x=x_2$ decreases by a ratio of $\exp(-e|V|/kT)$. As a result, protons flow out from the region II by diffusion. However, this current is small and soon attains saturation because of the low density of protons in this region.

These considerations explain the observed results well. Using the values of the parameters in Eq. 1 and those of the specific resistance of each membrane, 5×10^3 ohm·cm. for the cation-selective membrane and 4.5×10^3 ohm·cm. for the anion-selective membrane, and assuming $r_{\rm n}=r_{\rm m}$, we can estimate the parameters in the above equations. The results are given in Table I.

Although most of the values estimated above seem to be reasonable, there are many discrepancies. That is, the theoretical value of α in Eq. 1 is 38.6, while the observed value is 0.49. The rate of the dissociation of water into hydrogen and hydroxide ions has been observed to be 2.6×10^{-5} sec^{-1},[4] from which the rate of the thermal generation has been calculated as 1.56×10^{16} cm^{-3} sec^{-1}, while the present value is 6.7×10^{20} cm^{-3} sec^{-1}. Moreover, the rate of the recombination of hydrogen and hydroxide ions into water has been observed as 1.3×10^{11} l. mol^{-1} sec^{-1},[3] from which the mean-life time has been calculated to be 5.65×10^{-9} sec. for protons and 1.11×10^{-8} sec. for hydroxide ions, while the estimated values are 6.6×10^{-12} and 1.3×10^{-11} sec. respectively.

However, these disagreements are caused not by wrong treatments, but by the roughness of the model and unexpected errors in the experiments.

The final Eq. 13 is the same as Shockley's equation[5] for the p-n junction diode of semiconductors. This means that the same rectification mechanism holds true for the present system, with ionic charge-carriers, as for the semiconductor diode with electronic charge-carriers. Accordingly, the cation-selective membrane corresponds to the n-type semiconductor and the anion-selective membrane, to the p-type semiconductor. Moreover, it may be very instructive to consider hydrogen and hydroxide ions as protons and proton-defects respectively. By this analogy, most of the properties of the charge-carriers in the present ionic system might be understood by the methods used in the solid state physics, where the electron and its defect play an important role.

Summary

The electrolytic rectification effect has been observed in a double-membrane system. The static and dynamic current-voltage characteristics have been measured, and it has been demonstrated that the mechanism of the rectification similar to that of the p-n semiconductor junction holds true for this system. Reasonable values have been estimated for the characteristic parameters, although there are many discrepancies requiring further examination.

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[4] M. Eigen and L. De Mayer, *Z. Elektrochem.*, 59, 986 (1955).

[5] W. Shockley, "Electrons and Holes in Semiconductors," D. Van Nostrand Co., New York (1950), p. 309.