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Electron Transport and Redox Chain Reactions in a Mosaic Membrane

Manabu Igawa,[*] Yasuhiko Takabayashi,[†]
and Toshiaki Koizumi
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221
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A circulating current enhances transports of ions and electrons in a mosaic membrane system with ion-exchange membranes and electron-transport membranes. Electron transport is readily coupled to ion transport in a new mosaic membrane with electron-transport regions and ion-exchange regions. Electrons and ions are transported in the same or opposite direction by the driving forces of the redox potential gradient or the concentration gradient. Redox chain reactions are also generated in the mosaic membrane system as the electron flow in biological membranes.

Redox reaction is an electron-transfer phenomenon and is coupled to ion transport in vivo on the basis of chemiosmotic coupling[1] but the mechanism has not been fully clarified until now. It is difficult to realize the coupling phenomenon in an artificial membrane system, although there have been some reports on carrier mediated electron and cation transport across liquid membranes.[3–4] We have already reported a preliminary result of the coupling of redox reaction to ion transport in a new mosaic membrane system with an electron-transport membrane and ion-exchange membranes.[5] The electron transport is readily coupled to ion transport in the mosaic membrane system without a specific carrier. The electron transport accompanied by redox reactions causes an ion transport in this system similar to the chemiosmotic coupling in biological systems.[6]

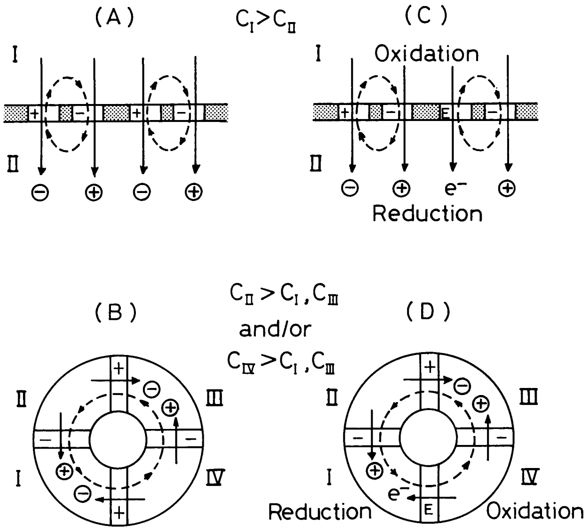

Fig. 1. Schematic circulating current in conventional mosaic membrane (A), in conventional mosaic membrane system (B), in novel mosaic membrane (C), and in novel mosaic membrane system (D). (+): Anion-exchange region or membrane, (−): Cation-exchange region or membrane, (E): Electron-transport region or membrane, (---): Circulating current, ⊕: Cation, ⊖ : Anion, e⁻: Electron.

Figure 1(A) shows the scheme of ion transport across a mosaic membrane proposed by Sollner.[7] A mosaic membrane has cation-exchange regions and anion-exchange regions, cations are permeated across the cation-exchange regions, anions are permeated across the anion-exchange regions, and consequently, circulating currents are generated across the membrane. The circulating currents in the mosaic membrane enhance ion transport and salts can be enriched under a pressure gradient by the mosaic membrane, which is called piezodialysis.[8] The membrane is, however, very difficult to be prepared because the opposite charged groups are arranged closely and alternately in the membrane. We have developed a mosaic membrane system,[9] where anion-exchange membranes and cation-exchange membranes are alternately arranged, and a circulating current is generated in the system as shown in Fig. 1(B). When all of the membranes in this system are cation-exchange membranes or anion-exchange membranes, ions are permeated through the imperfection of the membrane and the flux is very small. When cation-exchange membranes and anion-exchange membranes are arranged alternately, a circulating current generated in the cell causes a large ion flux.

If one of the anion-exchange membranes in the system is exchanged to an electron-transport membrane where ions can not be permeated but electrons can be permeated, electrons instead of anions are permeated across the membrane and a circulating current is generated in the new mosaic membrane system as shown in Fig. 1(D). The flux of the symbol, e⁻, in the Figure means electron current in the membrane. In this system, a reduction reaction occurs in the compartment I, an oxidation reaction occurs in the compartment IV, and cations are transported across the cation-exchange membranes to maintain the electric neutrality. Figure

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[†] Present address: Kurita Central Laboratories, Kurita Water Industries Ltd., Wakamiya, Morinosato, Atsugi 243-01.

1(C) shows electron and ion transport scheme in a novel mosaic membrane composed of ion-exchange regions and electron-transport regions. In this Figure, the solutes are oxidized in the upper part and reduced in the lower part. Electron-transport region or membrane is necessary to couple redox reaction to ion transport in both biological and artificial membrane. In the novel mosaic membrane or the novel mosaic membrane system, ion is transported by the driving force of the redox reaction which functions as a galvanic cell and the membrane potential causes electrolysis. The mosaic membrane or the mosaic membrane system is very simple and will be applied to give rise to many reactions.

In this paper, we will give a report concerning electron and ion transport across a novel mosaic membrane with an electron-transport region and an ion-transport region. We will also report the electron transport chain in a novel mosaic membrane system containing some electron transport membranes in which the redox chain reactions are achieved. Similar phenomena occur in phosphorylation in biological membranes, where protons play an important roll as ions. The system under examination simulates the electron flow in biological membranes in a simple manner.

Experimental

Apparatus. We used a flow-type dialysis cell with two compartments divided by the new mosaic membrane which was composed of an electron-transport region and an anion- or a cation-transport region as shown in Fig. 2(A). In this paper, commercial strong acid or strong base type ion-exchange membranes for electrodialysis, Selemion AMV and CMV manufactured by Asahi Glass Co. Ltd., and platinum plates were used as the ion-transport regions and the electron-transport regions, respectively. A mosaic membrane with electron and ion transport regions was constructed with a pair of membranes (an ion-exchange membrane and a platinum plate); these membranes were placed side by side in the same manner as the double carrier membrane system[10] and were fastened from either side of the membranes with an acrylic frame with two apertures, whose area was 7 cm^2 for each membrane. Each solution in the compartments divided by the mosaic membrane was pumped at a rate of 26 cm^3 min^{-1} from a reservoir to the compartment.

A simple redox reaction comprising a reduced state ion, an ion in its oxidized state, and a common counter ion is generated across the mosaic membrane. A redox chain reaction, however, requires a cell containing some electron-transport membranes and we used a mosaic membrane system composed of five compartments divided by two electron-transport membranes and three ion-exchange membranes as shown in Fig. 2(B). The other experimental conditions were the same as those of the mosaic membrane.

Dialysis. Some ions were transported from one compartment to the other adjacent compartment across the membrane under the driving force of the membrane potential or the redox potential difference. The ion and electron transport in the cell is evaluated in this paper by the change of concentration of potassium ion measured with an atomic absorption spectrophotometer and that of hexacyanoferrate(II) ion to hexacyanoferrate(III) ion and vice versa measured with a spectrophotometer at 420 nm.

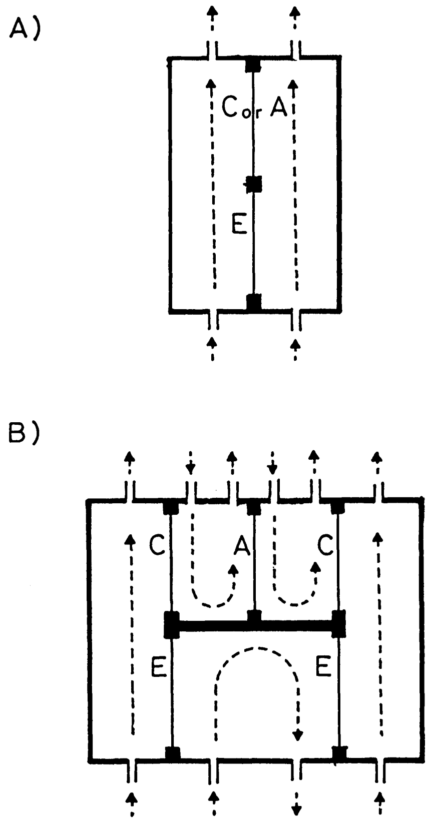

Fig. 2. Schematic representation of the cells of mosaic membrane (A) and mosaic membrane system composed of five compartments (B). A: Anion-exchange region, C: Cation-exchange region, E: Electron-transport region, ---: Fluid circulation.

Results and Discussion

Electron Transport in a Mosaic Membrane. Figure 3(A) shows the representative mechanism of the transport of electrons accompanied by ions (symport) and of electrons in one direction in exchange for ions in the opposite direction (antiport) across the new mosaic membrane. When the membrane is composed of an anion-exchange region and an electron-transport region, anions are antiported with electrons, while cations are symported with electrons when the membrane is composed of a cation-exchange region and an electron-transport region. Electrons and ions are transported across a membrane to maintain the electric neutrality and a circulating current is generated across the membrane. Redox reactions occur at the surfaces of the electron-transport region and the solutes are reduced in compartment I and oxidized in compartment II. The ion concentration change in the compartments can be estimated from the ion flux calculated by the circulating current, I_{theor}, which relates to the total potential in this system, E_{T}, and the total resistance, R_{T}, as follows.

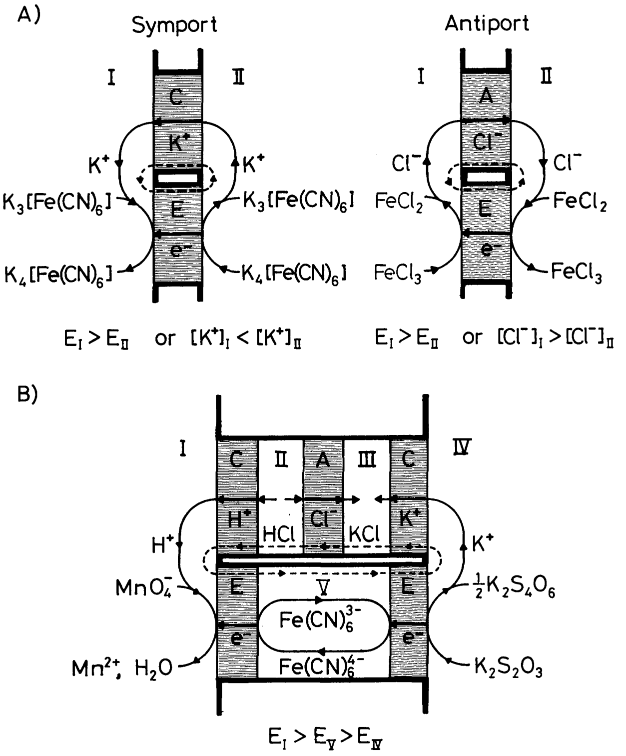

Fig. 3. Flows of electrons and ions in mosaic membrane (A) and in mosaic membrane system (B). A: Anion-exchange membrane, C: Cation-exchange membrane, E: Eelectron-transport membrane, I—V: Compartment number, ---: Circulating current, $E_{\mathrm{I-V}}$: Redox potential.

$$I_{\mathrm{theor}} = E_{\mathrm{T}}/R_{\mathrm{T}}, \tag{1}$$

$$E_{\mathrm{T}} = E_{\mathrm{I}} + E_{\mathrm{E}}, \tag{2}$$

$$R_{\mathrm{T}} = R_1 + R_2 + R_{\mathrm{I}} + R_{\mathrm{E}}, \tag{3}$$

where E_{I} and E_{E} are the membrane potential across an ion-exchange region and the redox potential difference across an electron-transport region, R_1 and R_2 are the solution resistances in compartment I and II, and R_{I} and R_{E} are the resistances of the ion-exchange region and the electron-transport region, respectively. The ion flux, J, is defined by Eq. 4 and the theoretical ion flux, J_{theor}, can be estimated from Eq. 5.

$$J = \mathrm{d}C\cdot V/(S\cdot \mathrm{d}t), \tag{4}$$

$$J_{\mathrm{theor}} = I_{\mathrm{theor}}/(n\cdot F\cdot S), \tag{5}$$

where C and V are the concentration and the volume of the solution of a compartment, respectively, S is the membrane area, t is time, n is the valence of the ion, and F is the Faraday constant. Since the circulating current can be represented as the function of the concentration using Eqs. 1—3 and the theoretical ion flux can be calculated by Eq. 5, the concentration change with time can be estimated by the integration of Eq. 4.

Figure 4 shows the concentration change of hexacyanoferrate(II) ion in compartment I and II. Potassium ion is symported with electron in the membrane with a cation-exchange region and an electron-transport region under a redox potential difference as shown in the left hand side of Fig. 3(A). Chloride ion was also antiported with electron in the membrane with an anion-exchange region and an electron-transport region under a redox potential difference as shown in the right hand side of Fig. 3(A). The increment of hexacyanoferrate(II) ion concentration in compartment I was equal to its reduction in compartment II. In this experiment, the theoretical membrane potential difference, E_{I}, and the theoretical redox potential difference, E_{E}, are defined by Eqs. 6 and 7 and R_{T} can be calculated by Eq. 8.

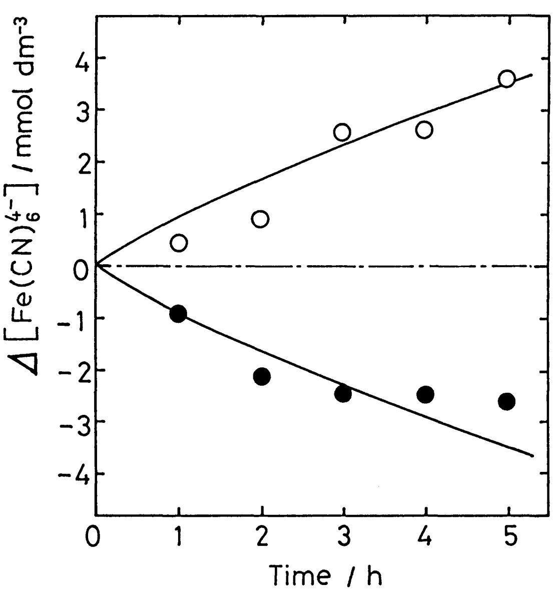

Fig. 4. Coupling of ion transport to electron transport in a mosaic membrane. ○: Concentration change in compartment I, ●: Concentration change in compartment II, —: Calculated values, compartment I: 2.94 mmol dm^{-3} $K_4Fe(CN)_6$ and 29.4 mmol dm^{-3} $K_3Fe(CN)_6$, compartment II: 23.3 mmol dm^{-3} $K_4Fe(CN)_6$ and 2.33 mmol dm^{-3} $K_3Fe(CN)_6$, each membrane area: 7 cm^2, each solution volume: 50 cm^3.

$$E_{\mathrm{I}} = RT/F\cdot\ln([\mathrm{K}^+]_{\mathrm{II}}/[\mathrm{K}^+]_{\mathrm{I}}), \tag{6}$$

$$E_{\mathrm{E}} = RT/F\cdot\ln([\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{II}}/[\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{II}}) - RT/F\cdot\ln([\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{I}}/[\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{I}}), \tag{7}$$

$$R_{\mathrm{T}} = (3.7/k_{\mathrm{I}} + 3.7/k_{\mathrm{II}})/S, \tag{8}$$

where R is the gas constant, T is the absolute temperature, the value, 3.7, is the distance (cm) between the regions in each compartment, and k is the electric conductivity of the solution I or II. The electric conductivity is the product of the equivalent concentration and the literature values[11)] of the equivalent conductivity of potassium hexacyanoferrates. The resistances of ion-exchange membranes as well as the resistance of platinum plate can be ignored comparing with the solution resistances because the ion-exchange membrane resistances are reported to be 2.0—3.5 ohm cm^2.[12)] The theoretical concentration changes in both compartments were calculated by using Eqs. 1—8. The initial rate of the concentration change can be calculated from the flux defined in Eq. 5 by using the initial concentration but the transported amount reflects the decrease of the redox potential difference and causes the membrane potential to be minus value to the circulating current. Then, the rate of the concentration change decreases with time. The experimental values (circles) closely follow the contours of the theoretical values (solid lines) and the values can be estimated theoretically.

Redox Chain Reactions. Redox chain reactions occur in the mosaic membrane system containing two electron-transport membranes as shown in Fig. 3(B). The redox potential of compartment I was the highest, that of compartment IV was the lowest, and the driving force of the ion transport was the redox potential difference between compartment I and IV. Electrons were transported from compartments IV to V across an electron-transport membrane, mediated by the hexacyanoferrate(II) ion in compartment V, and transported from compartment V to I. Figure 5 shows the results of electron and ion transport in the systems with and without compartment V. The electrons transported in the five-compartment cell including compartment V were larger in quantity than those transported in the four-compartment cell not including compartment V. The experimental value is much smaller than that estimated theoretically. Then, the coupling efficiency is defined for estimating the coupling of an electron transport with an ion transport in the system as the ratio of the measured ion flux to the theoretical ion flux as Eq. 9.

$$\text{Coupling efficiency} = J_{\text{measured}}/J_{\text{theor}}. \tag{9}$$

The theoretical ion flux can be calculated from the equations similar to Eqs. 1—5 except for the number of the compartments. In the experimental conditions of Fig. 4, the efficiency was about 1.0 but the efficiencies in the experiment of Fig. 5 were low. The efficiency was lowered by an overpotential generated at the surface of the electron-transport membrane. The effective driving force in the system was a product of the efficiency and the total potential difference. The coupling efficiency was higher in the redox chain reaction system in the five-compartment cell than in the single redox reaction system in the four-compartment cell as shown in Fig. 5. The redox potential difference across an electron-transport membrane was decreased by interposing the solution of an intermediate redox potential between compartments IV and I.

With the decrease of the potential difference across an electron-transport membrane, the coupling efficiency increased. The efficiencies measured in the four-compartment cell were 0.10 for 1.07 V (for the redox

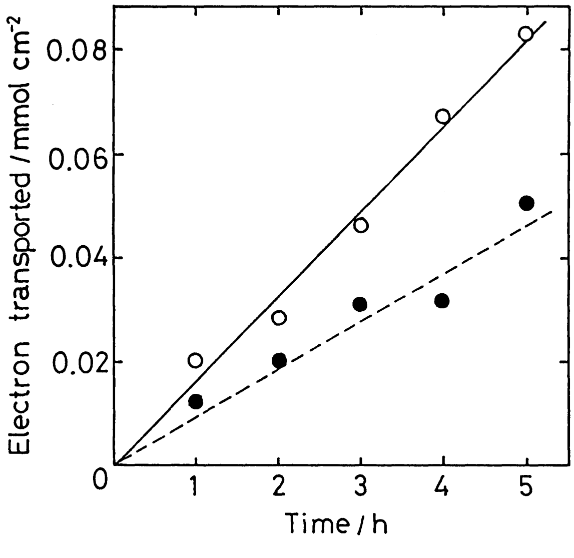

Fig. 5. Redox chain reaction in mosaic membrane system. ○: Electron transported in the five-compartment system with compartment V, (—): Calculated values assuming the coupling efficiency to be 0.17, ●: Electron transported in the four-compartment system without compartment V, (---): Calculated values assuming the coupling efficiency to be 0.10, compartment I: 10 mmol dm^{-3} $KMnO_4$ and 90 mmol dm^{-3} HCl, compartment II: 100 mmol dm^{-3} HCl, compartment III: 100 mmol dm^{-3} KCl, compartment IV: 50 mmol dm^{-3} $K_2S_2O_3$, compartment V: 18.2 mmol dm^{-3} $K_3Fe(CN)_6$ and 182 mmol dm^{-3} $K_4Fe(CN)_6$, each membrane area: 7 cm^2, each solution volume: 50 cm^3.

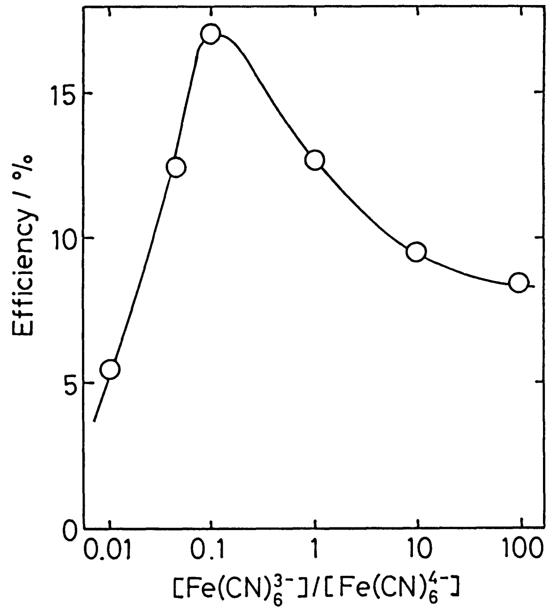

Fig. 6. Effect of the composition in compartment V on coupling efficiency. Compartment I: 10 mmol dm^{-3} $KMnO_4$ and 90 mmol dm^{-3} HCl, compartment II: 100 mmol dm^{-3} HCl, compartment III: 100 mmol dm^{-3} KCl, compartment IV: 50 mmol dm^{-3} $K_2S_2O_3$, compartment V: mixed solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (the total concentration was 200 mmol dm^{-3}), each membrane area: 7 cm^2, each solution volume: 50 cm^3.

potential difference of $MnO_4^-/Mn^{2+}—S_2O_3^{2-}/S_4O_6^{2-}$), 0.13 for 0.83 V (for $MnO_4^-/Mn^{2+}—Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$), and 0.29 for 0.24 V (for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}—S_2O_3^{2-}/S_4O_6^{2-}$). In Fig. 5, the effective driving force is calculated to be 0.107 V for the four-compartment system and that for the five-compartment system is 0.178 V, which is the sum of the effective driving force between compartments I and V, 0.108 V (0.13×0.83 V), and that between compartments V and IV, 0.070 V (0.29×0.24 V). The redox chain reaction system in the mosaic membrane system is simulating a biological process, such as the electron-transport chain of mitochondria arranged according to their midpoint potentials.[13] The redox chain reaction system was shown to be superior to the single reaction system and this electron-transport chain may exist in biological processes on the basis of a similar principle.

In the chain reaction system, the coupling efficiency increased with the increase of the concentration of the solution in compartment V and it also depended on the composition of the solution. The efficiency was the highest when the molar concentration of hexacyanoferrate(II) ion was 10 times higher than that of hexacyanoferrate(III) ion as shown in Fig. 6 because the reduction rate of permanganate ion in compartment I is low. In the system, permanganate ion oxidizes hexacyanoferrate(II) ion via an electron-transport membrane and thiosulfate ion reduces hexacyanoferrate(III) ion via another electron-transport membrane. With the increase of the reducing reagent (hexacyanoferrate(II) ion) concentration, the reduction of permanganate ion in compartment I was enhanced and the coupling efficiency increased but the efficiency became low when the concentration of the oxidizing reagent (hexacyanoferrate(III) ion) to thiosulfate ion was too low.

Electron transport is readily coupled to ion transport and the redox chain reactions are generated in a novel mosaic membrane system and the system simulates in a simple way the electron flow in biological membranes.

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