

## **Ion transport through diffusion layer controlled by charge mosaic membrane**

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### **ABSTRACT**

The kinetic transport behaviors in near interface of the membranes were studied using commercial anion and cation exchange membrane and charge mosaic membrane. From chronopotentiometry above the limiting current density, the transition time was estimated. The thickness of boundary layer was derived with conjunction with the conventional limiting current density and the transition time from steady state flux. On the other hand, the charge mosaic membrane was introduced in order to examine the ion transport on the membrane surface in detail. The concentration profile was discussed by the kinetic transport number with regard to the water dissociation (splitting) on the membrane surface.

Keywords: Ionic transport, Chronopotentiometry, Charge mosaic membrane, Thickness of diffusion layer, pH change

### **1. INTRODUCTION**

The aim will be focused on the ionic behavior of ion transport from bulk solution to membrane surface. In addition, so far developed charge mosaic membrane<sup>1-6)</sup> is introduced into electro dialysis model system and the ion transport mechanism is investigated. As experimental strategies, electrical methods were mainly adopted, and 4 kinds of membrane systems were selected to study; cation exchange membrane system(CMV), anion exchange membrane system(AMV), cation exchange membrane and charge mosaic membrane system(CMV+MM), and charge mosaic membrane and anion exchange membrane system(MM+AMV). It was examined how the charge mosaic membrane change the depleted solution layer and what kind of contribution the added membrane give for a membrane phenomenon.

The potentiometry was also used on the same membrane systems to elucidate the diffusion layer. The chronopotentiometry has been carried out to obtain the transition time<sup>7-9</sup>). The technique was adopted for 4 membrane arrangements to examine the contribution to the boundary layer of the charge mosaic membrane. The kinetic parameter about the boundary layer was noticed and introduced for understanding of the experimental results. The boundary layer thickness was already studied using chronopotentiometric technique in the underlimiting current-range<sup>10</sup>) but in this paper different other methods were adopted to measure the boundary layer thickness.

## **2. EXPERIMENTAL**

### **2.1. Materials**

The membranes used in the experiments were commercial Selemion CMV as cation exchange membrane, Selemion AMV as anion exchange membrane (Asahi glass.Co) and charged mosaic membrane MM which was developed in Dainichi Seika.Co. and contained both cation exchange group and anion exchange group fixed in the direction perpendicular to the membrane surface<sup>4-6</sup>). The KCl solution was prepared from  $10^{-5}$  to  $10^{-1}$  mol dm<sup>-3</sup> in this study.

### **2.2. Apparatus**

The main apparatus in this study is The potentiostat (Potentiostat/Galvanostat, HA-151, Hokutodenko. Co.). Chronopotentiogram was driven with a function generator (function generator, HB-111, Hokutodenko.Co.) and recorded by X-Y-t recorder (XY recorder F-35C, Riken Denshi.Co.). The experimental cell for the current-voltage measurement and the chronopotentiometry was the four-electrodes cell. The voltage drop across the membrane under investigation is measured by Haber-Luggin capillaries in which 3 M KCl solution was filled with agar and each connected to potentiostat or galvanostat where Ag/AgCl electrode was connected as reference electrode.

### **2.3. pH measurement**

pH indicator, phenolphthalein and methylred were put into the KCl solution to check simply the occurrence of water dissociation in the operation of chronopotentiometry. It was verified that the qualitatively pH change take place from slight red color.

## **3.RESULTS and DISCUSSION**

### 3.1. Transition time

The result of Chronopotentiogram in 0.01M KCl solution with using CMV was shown in Fig.1.

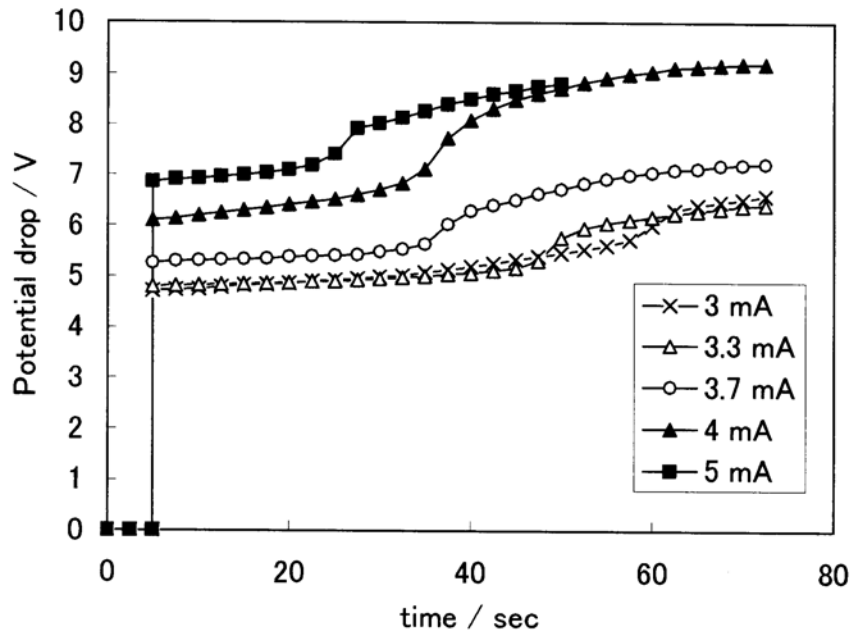


Fig 1. Chronopotentiogram with a cation exchange membrane in 0.01 M KCl solution.

Current densities are inserted in the figure.

All current densities imposed for the chronopotentiometry were always larger than the limiting current density obtained by the current-voltage curve measurement. In the case where such a large current was imposed on the membrane system, the concentration polarization should occur rapidly on the membrane surface and the concentration on the membrane surface becomes zero immediately. The transition time,  $\tau$  was defined as the time when the concentration on the membrane surface became zero.

Now, the transition time is given by Sand as following equation<sup>11-13</sup>.

$$\tau = \frac{\pi D_{KCl}}{4} \frac{1}{i^2} \left( \frac{Fz_i C_0}{t_i - t_i} \right)^2 \quad (1)$$

Here D is the diffusion coefficient of electrolyte,  $C_0$  and  $z_i$  the concentration in the bulk

and the charge of the counter ion,  $\bar{t}_i$  and  $t_i$  the transport number of the counter ion in the membrane and solution respectively,  $i$  the current density,  $F$  the Faraday coefficient. Then the measured transition times were indicated as a function of inverse of square of current densities in Fig.2. According to Fig.2, there were hardly difference between CMV and AMV membrane arrangements. On the other hand, in the case where the

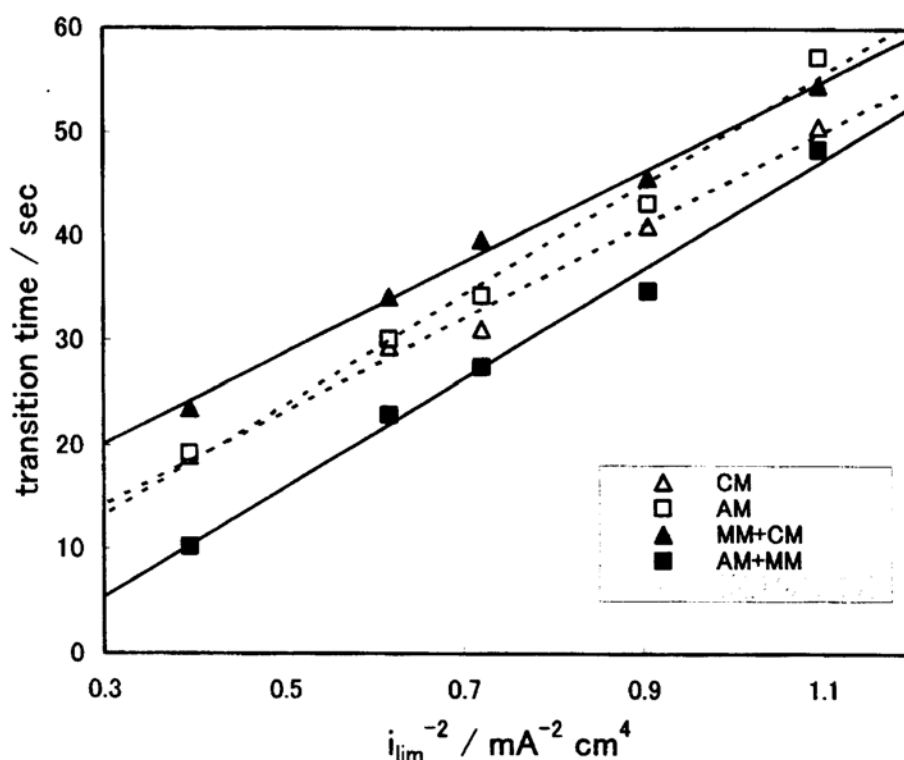


Fig.2. Transition time v.s.  $i_{lim}^{-2}$  in 0.01 M KCl solution. Symbols are inserted in the figure.

charged mosaic membrane was introduced additionally on cation- and anion exchange membrane like arrangements, MM+CMV and AMV+MM, the transition time was changed remarkably. The transition time,  $\tau$  increased on the arrangement, MM+CMV, while  $\tau$  on the arrangement, AMV+MM decreased. At present, it is not clear, but there seems to be influence of boundary layer,  $\delta$ .

### 3.2. Kinetic transport number in boundary layer

Eq. (1) was rearranged to evaluate the transport number at the boundary layer in the case of KCl solution as following.

$$t_i = \bar{t}_i - C_o F \frac{1}{i} \sqrt{\frac{\pi D_{KCl}}{4\tau}} \quad \text{where } z_i = 1 \quad (2)$$

Potential changes along the time and increases after the current density value reached on the transition time. The fact suggests that any ion transport process also changes after the transition time. The transport number might be changed under such a condition although the transport number had been almost unity in membrane when the relation between the voltage and the current has been simply ohmic at the moment. The kinetic transport number on the membrane surface was defined and derived from the above Eq.(2) on the moment when ion concentrations on the membrane reached zero.

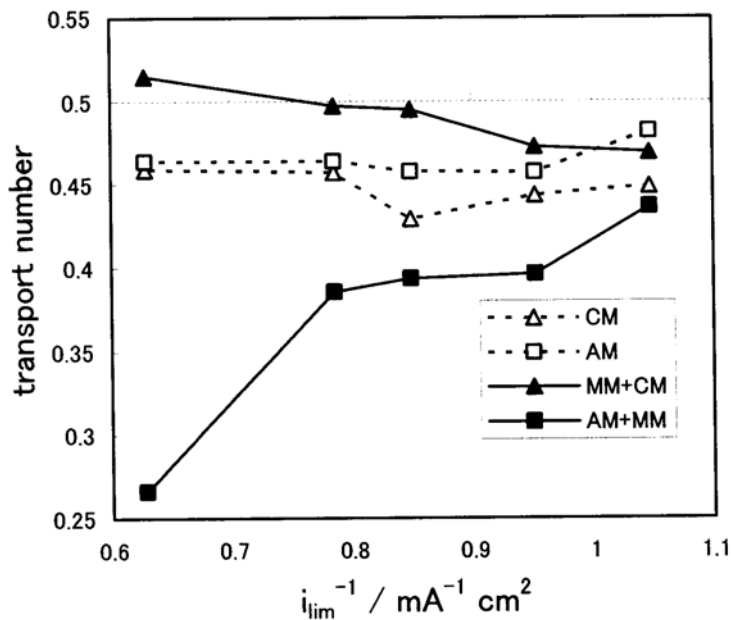


Fig.3. The change of transport number with various  $i_{lim}^{-1}$  value in 0.01 M KCl solution. Symbols are inserted in the figure.

The kinetic transport number in the boundary layer was shown in Fig.3, where the diffusion coefficient was assumed to be constant values in KCl solution and also transport number in membrane,  $\bar{t}_i = 1$ . An addition of the charged mosaic membrane resulted in the change of transport number at the boundary layer and the transport number tended to change remarkably with the extent of current density. Especially it

was supposed that the kinetic transport number in the boundary layer decreased remarkably in the case of AM+MM. Hence we define the transport number as kinetic transport number in boundary layer.

### 3.3.Thickness of boundary layer

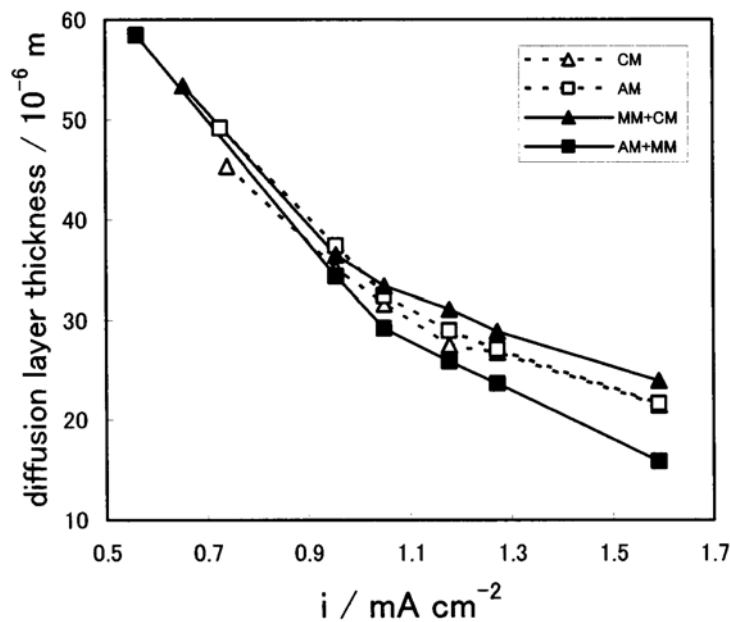


Fig.4. Diffusion layer thickness v.s. current density. Symbols are inserted in the figure.

Expression on the limiting current density was rearranged to derive the thickness of boundary layer as following<sup>14)</sup>.

$$\delta = \frac{FD_{KCl}C_o}{i_{lim}(t_i - t_i)} \quad (3)$$

The estimated limiting current density was already given in Fig.3. The transport number on designated ion should be unity through the membrane. This condition was equivalent with that in the chronopotentiometry at the transition time just before. It was supposed that the transport number and the current density obtained from the chronopotentiometry were able to be substituted by using Eq. (3) because the conditions on the surface of membrane are same. Then, the thickness of the boundary layer was represented in Fig.4. The added charge mosaic membrane caused the increase of the

thickness of boundary layer on the cation exchange membrane and the decrease on the anion exchange membrane. The tendency of change became remarkable depending on the current density.

Finally, it was suggested that the introduction of the charge mosaic membrane into ion exchange membrane resulted in the change of boundary layer's thickness and this results supported the speculation in 3.3. Transition time.

### 3.4. Water splitting

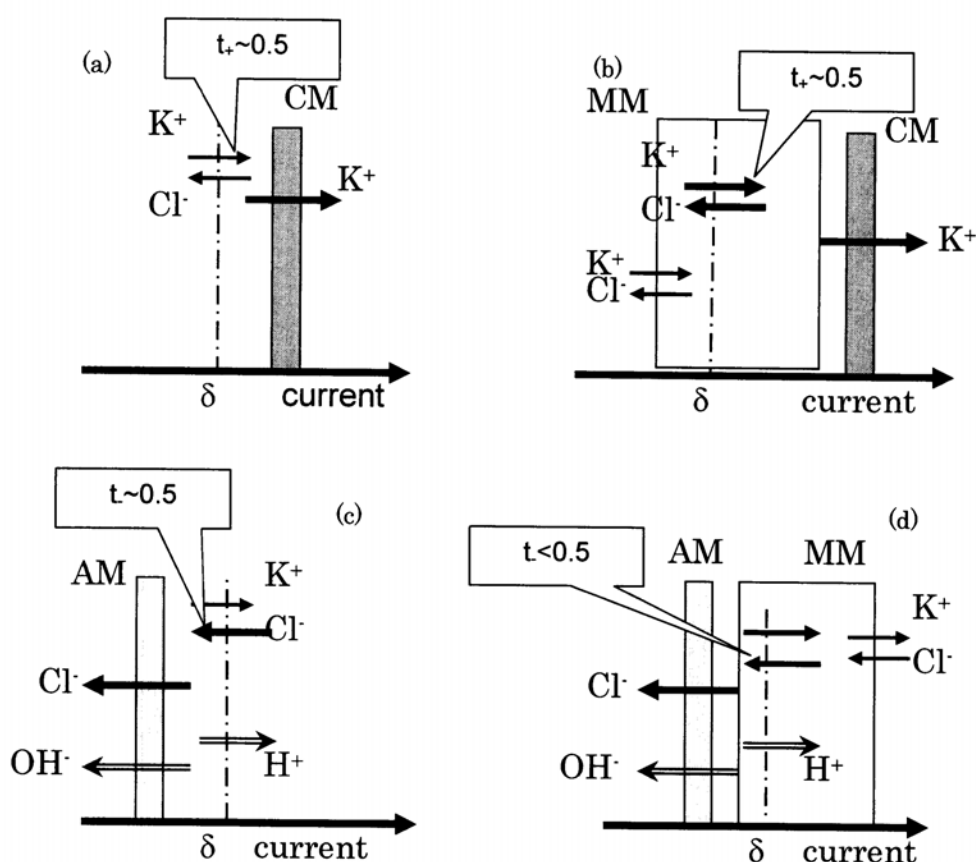


Fig.5. Schematic picture of ion transport on the membrane surface.

Incidentally the chronopotentiometry was carried out in the presence of pH indicator with the high current density on which the transport number was remarkably changed. The color in the solution did not change to red on the surface of cation exchange membrane, while the color changed to red on the anion exchange membrane. When the charge mosaic membrane was introduced on these membrane systems respectively, the

color changed as well. The pH indicator suggested that the water splitting occurred only on the anion membrane surface. The water splitting seemed to contribute to the transport number on the membrane surface. Then the phenomenon was examined with the following model in Fig.5.

## CONCLUSION

Kinetic transport number on ionic transport in the diffusion layer in near the membrane surface was obtained by means of the chronopotentiometry. The equation was developed to obtain the thickness of the diffusion layer from equation of limiting current density. The diffusion layers were indicated as function given current densities.

On the other hand, the water splitting phenomenon was observed from pH measurement in the both cases of anion exchange membrane system and anion exchange + charge mosaic membrane system. The phenomena together with relation to the thickness of diffusion layer were considered schematically in Fig.9.

In this study, it was examined whether the limit of current density could be increased by introducing the charge mosaic membrane.

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