일반강연 A-6

전류-전압곡선에 의한 이온교환막의 특성 분석

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Characterization of ion exchange membranes by current-voltage curves

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1. Introduction

It is common knowledge in electrodialysis that the current-voltage (I-V) curves of ion-exchange membrane have an "S" shape. Normally three regions can be observed in the curves: the first region of approximately ohmic behavior, the second region corresponding to the "plateau," followed by the third region of rapid current increase[1, 2, 3].

The classical theory of concentration polarization, based upon the concepts of an "unstirred" layer and local electroneutrality, predicts a true saturation of the I-V curve. As a result, I-V curves may provide important information about the mechanism of ion transport within the membrane and the characteristics of the ion transport.

The purpose of this study is to characterize an ion-exchange membrane using I-V curves. Basic equations for the potential drop in the membrane system were derived, and the parameters indicating the properties of the membrane system such as the diffusion boundary layer thickness, membrane resistance, and transport number of the membrane were determined by regressing the experimental data to the model equation.

2. Theory

For a membrane selective to specific ions, *i*, along with the assumption that the thickness, δ, of the both layers are equal, the current density, I, can be expressed by Eq.(1) [1]

$$I = \frac{FD(C_o - C_1)}{\Delta t_i \delta} = \frac{FD(C_2 - C_0)}{\Delta t_i \delta} \text{ --------------------------Eq.(1)}$$

where D is the salt diffusion coefficient, $\Delta t_i = t^m_i - t_i$, is the difference of transport number between the membrane and solution, and F is Faraday constant. When a constant current density is applied through the membrane system, the electric potential difference, Φ_T, between two fixed points placed on both sides of the membrane in the bulk solution is given by $\Phi_T = \Phi_o + \Phi_p$, where Φ_o is the potential drop before the polarization layers are formed and Φ_p is the potential drop caused by the formation of the polarization layer. These variables can be replaced by following equations.

$$\Phi_o = R_m + R_{so} = R_m + \frac{d - d_m}{\Lambda C_o} \text{ --------------------------------Eq.(2)}$$

$$\Phi_p = I\Delta R + \Phi_{Don} = \Lambda^{-1} \int_{-\delta}^{0} \left(\frac{1}{C(x)} - \frac{1}{C_o} \right) dx + \Lambda^{-1} \int_{d_m}^{d_m+\delta} \left(\frac{1}{C(x)} - \frac{1}{C_o} \right) dx + \frac{RT}{nF} \ln \frac{C_2}{C_1} \text{ ------Eq.(3)}$$

where, d is the distance between the reference electrodes, d_m membrane thickness, and Λ, the equivalant conductance of the electrolyte.

From Eqs. (1), (2), and (3) Eq.(4) can be obtained.

$$\Phi_T = \left(R_m + \frac{d - d_m}{\Lambda C_o} - \frac{2RT\Delta t_i \delta}{F^2 D C_o} \right) I + \frac{RT}{z_i F} \left(1 + \frac{1}{2\Delta t_i} \right) \ln \left(\frac{C_0 FD + \Delta t_i \delta I}{C_0 FD - \Delta t_i \delta I} \right) \text{ ------Eq.(4)}$$

Eq.(4) is applicable up to the limiting current density. From the data obtained in the ohmic region, the value for the boundary layer thickness and membrane resistance can be obtained for each experimental condition tested by fitting the data to Eq.(4).

3. Experimental

Current-voltage curves were obtained using a two-compartment cell at 25 ℃. This electrodialytic cell was composed of two equal volumn(150 ㎤) compartments. In the geometric center there was a cylindrical hole where the membrane is placed. The effective area of the membrane was 0.385 ㎠. Two Ag/AgCl reference electrodes were used to measure the potential difference between two membrane-solution interfaces. The electrical current was supplied by a potentiostat/ galvanostat (AutoLab, Model PGSTAT 30) connected to one pair of Ag/AgCl electrode sheets. Membrane resistance were measured by a clip cell at 10 kHz(LCZ meter, NF electronic instrument).

4. Results and Discussion

The I-V curves for the four different anion exchange membrane, AMX, AM-1, ACS, and ACM which were purchased from Tokuyama Soda, were studied under the same experimental conditions. The main characteristics of the membranes studied are listed in Table 1.

Table 1. The characteristics of the ion-exchange membranes studied[4].

Membranes	Properties	Electric resistance[a] (Ω/㎠)	Water content (g H_2O/g dry mem.)	Exchange capacity (meq/g dry mem.)
AMX	High mechanical strength	2.0-3.5	0.25-0.30	1.4-1.7
AM-1	Low electric resistance	1.3-2.0	0.25-0.35	1.8-2.2
ACS	Mono-anion permselective	3.0-6.0	0.20-0.30	1.4-2.0
ACM	Low proton transport	3.5-5.5	0.13-0.18	1.4-1.7

a) Electric resistance: Equilibrated with a 0.5 M NaCl solution at 25 ℃

Fig. 1 shows the I-V curves obtained without stirring. Each curve shows the three characteristic regions as expected. From the data obtained in the first region of the I-V curve, the values for the diffusion boundary layer thickness and membrane resistance can be obtained by fitting these data to Eq(4). Fig. 1 shows the result of the data regression together with the corresponding experimental values for the ACM membrane. With the proper parameter values, the experimental I-V curve agrees with the model equation, the results of which are reported in Table 2. As shown in Table 2, the values of R_m estimated by I-V curves were in agreement with the values measured by clip cell. This indicates that the membrane resistance was reasonably measured using the I-V curves.

Analysis of the membrane resistance shows that the ACS membrane has the highest resistance. The order of membrane resistance is AM-1<AMX≪ACM≅ACS. It also shows that this sequence is good agreement with the

characteristic of the membranes, as referred to in Table 1.

The limiting current density(LCD) can be calculated using Eq.(5) [5, 6]

$$I_L = \frac{F \cdot C_o \cdot D}{\delta \cdot \Delta t_i} \quad \text{-----------------------------------Eq.(5)}$$

Using the δ values estimated from the I-V curves, it was possible to calculate the LCD. The results are also shown in Table 2.

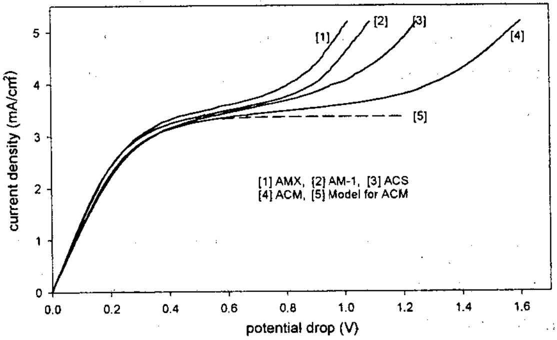

Fig. 1. I-V curves for different ion-exchange membranes

Table 2. The parameter values estimated for ion-exchange membranes.

membranes	R_m(Ω · cm²) (from I-V curve)	R_m(Ω · cm²) (from clip cell)	δ (cm)	LCD (mA/cm²)	Δt_i
AMX	27.27	28.13	0.02715	3.612	0.977
AM-1	23.12	24.28	0.02807	3.494	0.991
ACS	34.29	33.09	0.02811	3.489	0.991
ACM	29.31	31.48	0.02872	3.415	1.000

The boundary layer thickness is directly related to the stirring conditions of electrolyte solution[1]. According to Eq.(5), the limiting current density should be same if the concentration of the electrolyte and the mixing were maintained under the same condition. The results for the membranes, however, show some differences in LCD. This difference is due to the difference in the membrane transport number of the counter ion. Since ACM membrane is used to block proton leakage, it is expected that this membrane would have an ideal selectivity. Therefore, assuming that the real boundary layer thickness under this experimental condition is 0.02872 cm, the transport number for each membrane can be calculated by adjusting the parameters of R_m and Δt_i in Eq.(4). These results are also presented in

Table 2. The AMX and ACS membrane have close exchange capacities and water contents(Table 1), but the transport number for the ACS membrane is higher than for the AMX membrane. This is due to the effect of the surface modification of the ACS membrane which is designed to be mono-anion permselective. Also, the reason for the high permselectivity of AM-1 is that its exchange capacity is higher than the other membranes.

The parameter values of the ion-exchange membranes, R_m, δ and Δt_i estimated from the I-V curves can explain the properties of the each membrane. This new method is very simple but able to predict the characteristics of a membrane precisely.

5. Conclusion

To characterize the ion-exchange membrane, an equation that relates the voltage drop with the current in the membrane system while considering concentration polarization was derived. I-V curves determined for a Neosepta anion exchange membranes showed good agreement with the equation. The boundary layer thickness, membrane resistance, and transport number for each membrane could be determined by regressing the data according to the first region of the I-V curves. Further studies on characterization of water-splitting phenomena are going on.

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