THEORY OF THE CURRENT YIELD IN ALKALI PRODUCTION BY ELECTROLYSIS WITH A CATION-EXCHANGE MEMBRANE. THE TWO-LAYER MEMBRANE

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In an earlier communication concerning this topic [1] we have discussed the motion of ions across a homogeneous ion-exchange membrane. This process was described as the combination of diffusion and migration, and the latter was characterized by an effective mobility, u, which included a possible effect of liquid flow on the rate of motion of the ions (it is formally possible to include this effect, since the liquid flow across the membrane is proportional to current density). In this case the equation for the flow of OH^- ions can be written as

$$j = -D\frac{dc}{dx} + uEc. \tag{1}$$

It was shown in [1] that for ion-exchange membranes, the constant-field approximation, E = const, holds with good accuracy.

In this approximation, and with the boundary conditions

$$\begin{aligned} x=0,\quad c=c_0;\\ x=\delta,\quad c=0 \end{aligned} \tag{2}$$

the solution of Eq. (1) yields

$$c = c_0\frac{\exp(uE\delta/D) - \exp(uEx/D)}{\exp(uE\delta/D) - 1} \tag{3}$$

and

$$j = uEc_0\frac{\exp(uE\delta/D)}{\exp(uE\delta/D) - 1}. \tag{4}$$

Here, δ is the membrane thickness; the fraction in the right-hand side of Eq. (4) gives the diffusion correction for the purely migrational flow uEc_0. Quantity $uE\delta/D$ is close to $\Delta VF/RT$, where ΔV is the voltage drop in the membrane, so that for $\Delta V > 2.3$ RT/F the flow of OH^- ions practically equals the migrational flow, i.e., is minimal, while the current yield of alkali therefore is maximal [1]. It had been concluded on this basis in [1] that in order to achieve maximum current yield it will suffice to have a thin layer of a highly selective (and hence also relatively poorly conducting) membrane on the surface of a thicker and stronger membrane having good conductivity (but low selectivity). Under these conditions the voltage drop in the highly selective layer should be higher than 2.3 RT/F ≈ 70 mV (at the temperature of industrial electrolysis).

In fact, a tendency is seen recently to use two-layer membranes; in these, the thinner layer has a reduced concentration of immobile sulfo groups, and hence large selectivity [2, 3]. It is of interest in this connection to examine the flow of ions across such a two-way membrane.

In this case the motion of the ions will be described by Eq. (1), but each of the layers, of thicknesses δ_1 and δ_2, will have its own characteristic values of D, u, and E. The boundary conditions for the first layer are

$$\begin{aligned} x=0,\ c=c_{01},\\ x=\delta_1,\ c=c_{\delta 1}. \end{aligned} \tag{2a}$$

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The solution of (1) with these boundary conditions is

$$c=c_{01}\frac{a-\exp(u_1E_1x/D_1)}{a-1}, \tag{5}$$

where

$$a=\frac{c_{01}\exp(u_1E_1\delta_1/D_1)-c_{\delta 1}}{c_{01}-c_{\delta 1}}.$$

The expression for the flow of ions across the first layer is,*

$$j_1=\frac{a}{a-1}u_1E_1c_{01}. \tag{6}$$

The boundary conditions for the second layer,

$$\begin{aligned} &x=\delta_1,\ c=c_{02};\\ &x=\delta_1+\delta_2,\ c=0. \end{aligned} \tag{2b}$$

coincide with boundary conditions (2); hence for the second layer, Eqs. (3) and (4) are valid with the substitution of $(x - \delta_1)$ for x and with subscripts "2" in all constants.

It had been suggested in [1] that kinetic limitations do not exist at the membrane/solution interface, i.e., the alkali concentration, c_0, in the membrane at x = 0 is in equilibrium with the catholyte. The same is true for c_{01}. For c_{02}, which is the OH^- concentration at the start of the second layer, we shall assume that kinetic limitations also are absent at the interface between the two cation-exchange membranes, i.e., c_{02} is an equilibrium quantity with respect to $c_{\delta 1}$. Introducing the corresponding equilibrium constant

$$K=\frac{c_{02}}{c_{\delta 1}} \tag{7}$$

and allowing for continuity of the OH^- flow,

$$j_1=j_2=j, \tag{8}$$

we can now find the steady-state value of $c_{\delta 1}$:

$$c_{\delta 1}=\frac{u_1E_1c_{01}f_1(\delta_1)}{Ku_2E_2f_2(\delta_2)+u_1E_1\varphi_1(\delta_1)} \tag{9}$$

and the magnitude of the OH^- ion flow which governs the loss in alkali yield:

$$j=\frac{Ku_2E_2u_1E_1f_1(\delta_1)f_2(\delta_2)}{Ku_2E_2f_2(\delta_2)+u_1E_1\varphi_1(\delta_1)}c_{01}. \tag{10}$$

Here the following symbols were used:

$$f_i(\delta_i)=\frac{\exp(u_iE_i\delta_i/D_i)}{\exp(u_iE_i\delta_i/D_i)-1}$$

and

$$\varphi_1(\delta_1)=\frac{1}{\exp(u_1E_1\delta_1/D_1)-1}.$$

For two layers which are identical in their properties, i.e., with K = 1, $u_1 = u_2$, etc., Eq. (10) as expected changes into expression (4) for the flow across a single-layer membrane (with $\delta_1 + \delta_2 = \delta$). On the basis of Eq. (10) we shall now analyze the most important cases of ion transport across the bilayer membrane.

*One can readily see that solutions (3) and (4) are particular cases of (5) and (6) for $c_{\delta 1} = 0$.

We shall first evaluate certain quantities. Since always $uE\delta/D > 0$, one has $\exp(uE\delta/D) > 1$ and $f_i(\delta_i) \geqslant 1$. It has hardly any practical sense to consider layers which are so thin that the voltage drop across them is less than a few millivolts.* For $\Delta V = 35$ mV, one has $\exp(uE\delta/D) \approx 2.7$; $f(\delta) \approx 1.6$; $\varphi(\delta) \approx 0.6$. At large ΔV, quantity $f(\delta)$ is still closer to unity, while $\varphi(\delta)$ is still smaller. The ionic mobilities may be a few times different in different layers, but the electric field strengths will vary in approximately inverse proportion to the mobilities (see, e.g., Eq. (3) of [1]). Hence the products u_1E_1 and u_2E_2 are quantities of the same order of magnitude.

Consider now the first typical case, where the first layer (i.e., the part of the membrane turned toward the cathode) is more selective. This means that superequivalent alkali will be taken up much better by the second layer than by the first, i.e., $K \gg 1$. Considering the estimates made above for quantities $f(\delta)$, $\varphi(\delta)$, and uE, we then can conclude that the second term in the denominator of Eq. (10) can be neglected relative to the first, and Eq. (10) becomes appreciably simpler:

$$j \simeq u_1E_1c_{01}f_1(\delta_1). \tag{10a}$$

This equation is none other than Eq. (4) written for the first layer. Thus, if the more selective layer is arranged on the cathodic side, the current yield will practically be the same as that which one would obtain from a membrane consisting of this layer alone. With a sufficiently high voltage drop across this layer, the alkali loss would be determined by migration alone.

The physical meaning of this result can be explained as follows. With a sufficient layer thickness, diffusion has no effect on the OH^- ion flow at the membrane entrance. The OH^- concentration decreases with increasing distance from the cathodic surface, slowly at first but then more rapidly [see Eq. (5)], the migrational flow decreases, and the diffusional component increases accordingly. The same flow passes across the interface between the two layers, and the concentrations on both sides of the interface will assume values such that the flows will be equal. The concentration distribution is shown schematically in Fig. 1a. The drop at the interface corresponds to $K > 1$, i.e., the second layer can more actively absorb excess alkali. One can see from Eq. (9) that for $K \gg 1$ one has $c_{\delta 1} \approx c_{01}/K$, i.e., the concentration falls to a value many times smaller over the length of the first layer. Hence the concentration distribution is similar to that which one would have in the operation of a single-layer membrane ($c_\delta = 0$), and this case is shown as a dashed line. Near the membrane entrance these distributions are practically indistinguishable, so that the ion flow at the entrance and, therefore, the entire steady-state flow as well are practically the same in the two cases.

Strictly speaking, the sign of approximate equality in Eq. (10a) should be replaced by the sign $\leqslant$, i.e., the OH^- flow across the two-layer membrane is a little smaller than that across the single-layer membrane (we come to the same result when examining the concentration profiles). Thus, the current yield still becomes a little higher when the second layer is present, but this effect is very small and hardly noticeable in practice.

Consider now the other case where the more selective layer is arranged on the anodic side of the membrane, i.e., where $K \ll 1$. In this case the second term in the denominator of Eqs. (9) and (10) cannot be neglected (depending on the quantities K and $\varphi_1(\delta_1)$, it can even be larger than the first term). The ratio

$$\frac{u_1E_1f_1(\delta_1)}{Ku_2E_2f_2(\delta_2)+u_1E_1\varphi_1(\delta_1)} \gg 1,$$

since quantities of the same order of magnitude as the numerator which are multiplied by factors much smaller than unity are found in the denominator. It follows that

$$j > u_2E_2Kc_{01}f_2(\delta_2) \tag{10b}$$

i.e., the flow across the membrane is appreciably larger than that which one would have with the highly selective layer operating alone. In this case the two-layer membrane leads to a lower yield than the single-layer membrane. The reason for this result can be understood by examining the concentration profile (Fig. 1b). A considerably larger flow of ions is en-

*We recall that for the single-layer membrane, the current yield came close to a maximum when $\Delta V \gtrsim 70$ mV.

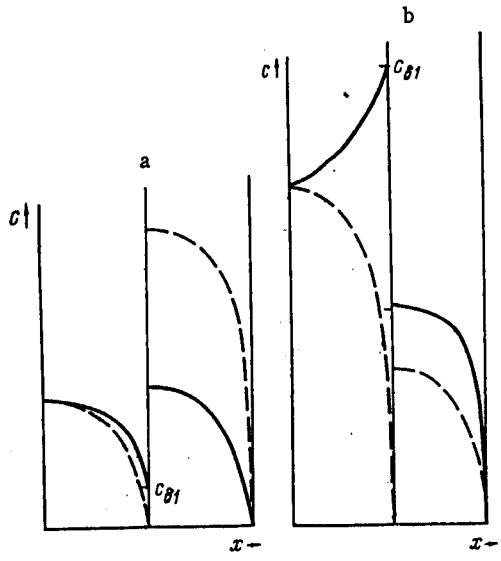

Fig. 1. The alkali concentration distribution across the membrane. The cathodic layer is more (a) or less (b) selective than the anodic layer. Dashed lines show the distribution for each of the layers in the case where the membrane consists of this layer alone.

tering the less selective layer by migration than can pass into the more selective layer. Hence alkali is accumulating at the interface between these layers and gives rise to a diffusional backflow of the OH^- through the first layer. Because of the alkali accumulation, the second layer is bordering a more concentrated solution than it would, were it in direct contact with the catholyte (the distribution for this case is shown by a dashed line). This produces a higher c_{02} value, and the migrational flow across the selective layer becomes stronger.

It also follows from Eq. (10) that for the case being considered,

$$j < u_1 E_1 c_{01} f_1(\delta_1), \qquad (10c)$$

i.e., the alkali flow is smaller than it would be with only the first, less selective layer operating. This can also be seen directly from the plots of the concentration distribution.

Thus, by placing the two-layer membrane so that the selective layer is toward the anode one obtains a somewhat better current yield than with the less selective membrane operating as a single-layer membrane, but one that is much inferior to that obtained with the selective membrane operating as a single-layer membrane. But by placing the selective side toward the cathode one obtains practically the same current yield (or a yield that is a trifle larger) as in the operation of the selective layer alone.

LITERATURE CITED

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