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

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The electrochemical production of pure alkalies with the use of homogeneous cation-exchange membranes is a very promising possibility for their industrial manufacture [1, 2]. In this method, the ion-exchange membrane separates the cathode compartment filled with pure alkali from the anode compartment containing weakly acidic NaCl solution. Through the membrane, Na^+ ions and water are transported in the cathodic direction, and OH^- ions are transported in the anodic direction. Diffusional transport of Cl^- ions in the cathodic direction is small as compared to the other flows, and can be neglected when examining the balance of the chief products. Under various electrolysis conditions one finds that OH^- ions are transferred into the anode compartment, so that the medium in the membrane is alkaline right up to the membrane's anodic side, and a flow of H^+ ions in the cathodic direction is therefore absent.*

Let us write down the equation for the steady-state flow of OH^- ions in the anodic direction (j_-) while regarding the homogeneous membrane as an isotropic medium

$$-D_-\frac{dc_-}{dx}+u_-^\circ c_- E-vc_-=j_-. \tag{1}$$

Here, D_- and u_-° are the effective diffusion coefficient and the mobility of the OH^- ion in the given medium, the x coordinate is counted from the cathodic to the anodic side of the membrane, c_- is the concentration of OH^- (a function of x), E is the electric field strength, and v is the liquid's counterflow velocity.

The counterflow of liquid is due to the development of hydrational and electroosmotic water transport. Experience shows that this transport is proportional to current density, i.e., $v = v^\circ E$. Hence Eq. (1) can be simplified, and written as

$$-D_-\frac{dc_-}{dx}+u_- c_- E=j_-, \tag{1a}$$

where $u_- = u_-^\circ - v^\circ = u_-^\circ\gamma$. Here γ is a quantity smaller than unity, but according to available data concerning the flow of water through membranes [3], it does not differ much from unity.

Let us write down the analogous expression for the flow of sodium ions:

$$+D_+\frac{dc_+}{dx}+u_+^\circ c_+ E+v^\circ c_+ E=j_+. \tag{2}$$

Here, c_+ is the concentration of Na^+ ions, which is given by $c_- + c_{ex}$; c_{ex} is the exchange capacity (i.e., the constant Na^+ ion concentration), which is given by the concentration of immobile anions attached to the polymeric matrix. Multiplying (2) by D_-/D_+ and adding the expression obtained to (1) we find the field strength as a function of the concentration of ions in any point:

$$E=\frac{j_-+\dfrac{D_-}{D_+}j_+}{\left[u_-^\circ+\dfrac{D_-}{D_+}u_+^\circ+\left(\dfrac{D_-}{D_+}-1\right)v^\circ\right]c_-+\dfrac{D_-}{D_+}(u_+^\circ+v^\circ)c_{ex}}. \tag{3}$$

*Even with highly selective membranes, i.e., a small flow of OH^- ions, the flow of H^+ ions is small as compared to that of Na^+ ions, since their concentration in the anolyte is at least 2.5 orders of magnitude lower.

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The factor of c_- in the denominator is of the same order of magnitude as that of c_{ex} (their ratio probably is a value $\lesssim 2$), but the concentration of nonexchange electrolyte in the membrane is substantially smaller than the membrane's exchange capacity, particularly in concentrated alkali solutions [4]. Therefore, even though c_- can change very strongly across the membrane, the corresponding term in the denominator of (3) is small as compared to the second term, which contains the constant quantity c_{ex}. Thus, the field is practically constant across the entire membrane, and in the following we can use the constant-field approximation.

The feasibility of this approximation is confirmed by the experimental observation that the voltage drop in the membrane is changing practically linearly with current density, i.e., obeys Ohm's law corresponding to E = const. Strictly speaking, the voltage drop being measured in the membrane is the sum of the voltage drop in the membrane itself and of the polarization at the membrane/solution interfaces. Preliminary results of membrane impedance measurements at different frequencies performed in our laboratory by R. G. Érenburg and A. V. Zhigunov show that the resistance of the membrane/solution interface is small as compared to the membrane's bulk resistance, so that the contribution of polarization to the total voltage drop can be neglected. Therefore, proportionality of the measured voltage drop to current density indicates that the potential distribution in the body of the membrane is ohmic in character.

Because of the low polarization at the interface, one can assume to a first approximation that the concentration of OH^- ions in the membrane is in equilibrium with the OH^- ion concentration in the adjoining solution, i.e., one can specify the boundary conditions as

$$\begin{aligned} x=0, \quad & c_-=c_0; \\ x=\delta \quad & c_-=0. \end{aligned} \tag{4}$$

Here c_0 is the OH^- concentration in the membrane which is in equilibrium with respect to the alkali concentration in the catholyte. On the anodic side ($x = \delta$), the membrane is bordering at a weakly acidic, or possibly a neutral or even a weakly alkaline, solution. However, the exact value of this OH^- concentration is not important for us; it suffices to know that it is negligibly small as compared to the catholyte concentration, and hence for $x = \delta$ one can assume that $c = 0$.

The solution of (1a) with boundary conditions (4) has the following form:

$$c_-=c_0\frac{\exp\frac{u_-E}{D_-}\delta-\exp\frac{u_-E}{D_-}x}{\exp\frac{u_-E}{D_-}\delta-1}. \tag{5}$$

The corresponding expression for the flow of OH^- ions is

$$j_-=u_-Ec_0\frac{\exp\frac{u_-E}{D_-}\delta}{\exp\frac{u_-E}{D_-}\delta-1}. \tag{6}$$

The flow of OH^- ions governs the loss in current yield. The current yield, as a fraction of unity, is given by

$$A=1-\frac{j_-F}{i}, \tag{7}$$

where i is the current density, and multiplication by F serves to translate the flow of OH^- ions into electrical units. Let us consider in more detail the structure of Eq. (6).

Quantity u_-Ec_0 is nothing but the migrational flow of OH^- ions across the membrane which would occur in a membrane entirely saturated with alkali of constant concentration. All the quantities contained in it — u_-, E, and c_0 — are determined by the properties of the membrane and, of course, by the concentration of the alkali bordering at the membrane [quantity E, in terms of the constant-field model, is defined as the product of the specific resistance ρ and current density i; ρ depends on the factors listed here, while i drops out of the expres-

sion (7) for the current yield in this factor]. The loss due to migration is the smallest of the losses possible for a given membrane and alkali concentration; OH^- ion diffusion can only increase this loss. This is taken care of by multiplying the migrational term by a fraction which, generally, is larger than unity. The exponential in Eq. (6) contains the quantity $E\delta = \Delta V$, which is the voltage drop in the membrane, and factor $u/D = \gamma u_0/D$. Quantity u_0/D can be replaced by F/RT, according to the Nernst–Einstein relation. In ion-exchange membranes, this law often is violated: the migration mobility is found to be larger than the diffusional mobility [5], which can be taken care of by a factor $\beta > 1$. Thus, we can rewrite (6) as

$$j_-=u_-Ec_0-\frac{\exp\frac{\Delta VF}{RT}\gamma\beta}{\exp\frac{\Delta VF}{RT}\gamma\beta-1}. \qquad (6a)$$

The factor $\gamma\beta$ most likely is somewhat larger than unity, but since we only want to know the order of magnitude of the quantities, we can set it equal to unity. One can see from (6a) that with voltage drops in the membrane substantially larger than RT/F, the fraction is close to unity, and the flow of OH^- practically coincides with the purely migrational flow, i.e., the current yield is maximal under these conditions (for a given membrane and specified alkali concentration). For example, with $\Delta V \approx 140$ mV, the corresponding exponential term is 10^2 at the temperatures used in industrial electrolysis, i.e., $j_- = u_-Ec_0 \cdot 1.01$ and the current yield is practically the same as the maximum yield. With a minimum loss of 20% in current yield, this loss becomes 20.2%. Even for $\Delta V \approx 70$ mV, the corresponding correction is 1.1, i.e., will again not be large. Under current operating conditions, the voltage drop in the membrane is between several tenths of a volt and 1 V [1]. This means that at a given current density, the membrane thickness can be reduced several times (of course, while preserving homogeneity and sufficient strength of the membranes) without any decrease in the current yield, but with a substantial saving of electric energy. But is is not advantageous to reduce the voltage drop in the membrane to a level below several tens of millivolts, e.g., 70 mV, since this produces a substantially lower current yield with only a relatively small gain in voltage. Further, it appears promising to provide the surface of sufficiently thick, and hence mechanically strong, yet well conducting and poorly selective membranes with a thin, highly selective layer of large specific resistance, which will guarantee a good current yield but will not cause an excessive growth of the voltage, because of the small thickness (ΔV in this case will be a few tens of mV).

LITERATURE CITED

1. N. R. Iammartino. Chem. Eng. (New York), 83, No. 13, 86 (1976).
2. H. Seya and J. Nakata, Chem. Econ. Eng. Rev., No. 9, 23 (1975).
3. G. A. Grishaeva, I. G. Gurevich, and V. S. Bagotskii, Élektrokhimiya, 10, 773 (1974).
4. N. I. Men'shakova, L. I. Krishtalik, and V. L. Kubasov, Élektrokhimiya, 13, 1732 (1977).
5. N. I. Nikolaev, A. M. Filimonov, and N. N. Tunitskii, Zh. Fiz. Khim., 43, 1249 (1969).