Short Communication

Nonstationary State in Countercurrent Electrolysis in a Porous Membrane

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Countercurrent electrolysis in a thin porous membrane can be used to separate ions of different mobilities both in systems consisting of strong electrolytes[1,2,3] and weak electrolytes.[4] A special multi-ion case, a binary electrolyte system with trace ions,[5] as well as the influence of the membrane thickness[6] have also been studied. While investigating the effect of the membrane thickness on separation efficiency, it was noticed that the rate of reaching the stationary state rapidly decreased when the membrane was made thicker. If the volume of the porous membrane is small compared to the volume of the compartment where the electrolytes are diffusing, it can be assumed that the fluxes across the membrane are stationary. In that case, the membrane is called thin and the mathematical modelling of the nonstationary state can be done rather easily; likewise, in multicomponent electrolyte systems. However, in practice, it is desirable to make the volume of the compartment as small as possible to avoid ohmic losses and obtain effective stirring when using forced-flow convection. Furthermore, it is preferable to use as thick a membrane as possible to increase separation efficiency. As a result, the assumption of stationary fluxes across the porous membrane fails.

In this paper, we first study the nonstationary stage in countercurrent electrolysis both in binary and ternary electrolyte systems in the case of a *thin* porous membrane; the transient behaviour is then studied in the case of a *thick* membrane when the electrolyte system is binary and a solution in closed form can be obtained. This solution makes it possible to evaluate the effect of the ex-perimental parameters on the attainment of stationary state across the membrane.

Countercurrent electrolysis in a porous membrane

Consider a system consisting of two electrolyte solutions (α and β) separated by a membrane (M) (see Fig. 1). The membrane is assumed to be of the wide pore type so that there is no specific interaction between the membrane and the electrolytes. The pressure difference determines the rate at which the solution flows through the porous membrane and the electromotive force and the resistance of the electric circuit determine the electric current. The electrolyte solutions in compartments α and β are kept homogeneous by stirring. When cations are separated, the polarity of the electric current is chosen as presented in the figure. Anion exchange membranes (AM) are used to separate the electrode compartments (E) from compartments α and β. The concentrations (c_i^β) in compartment β are kept constant by circulating the electrolyte solution being studied so rapidly that no essential changes in concentration take place. The water (or electrolyte solution) flowing into compartment α is denoted by V^o. Part of this flow passes out of the compartment as the product stream V^α while the rest flows as convection through the porous membrane $V^c = V^o - V^\alpha$.

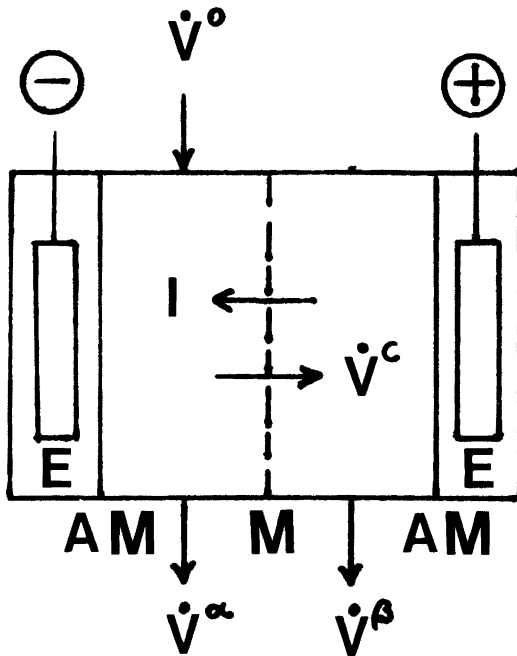$$V^\alpha \frac{dc_1^\alpha}{dt} = V^o c_i^o - V^\alpha c_i^\alpha - J_i A \qquad (1)$$

Fig. 1. Schematic drawing of the cell for countercurrent electrolysis in a porous membrane (V^α and V^β are volumes of the compartments).

In countercurrent electrolysis in a porous membrane, the ionic equivalent conductivities determine the order in which the ions are separated.[3] This means that the ions with greater equivalent conductance may be enriched from a mixture of electrolytes, the faster moving ions travelling more quickly against the convection $\dot{V}^c$. In the case of a *thin membrane*, the mass balance for cations (i) in the α compartment (Fig. 1) is given by eqn. (1) where V^α is the volume of the α compartment, c_i^α is the concentration of ion i in α compartment, t is time, c_i^o is the concentration of i

in $\dot{V}^o$, J_i is the flux of cation i, and A is the surface area of the porous membrane. Since the membrane is thin, it can be assumed that a quasi-stationary state continuously exists in the membrane.

In a binary electrolyte system, the flux J_i in eqn. (1) can be derived using the Nernst-Planck equations for the stationary state. The result for a 1,1 electrolyte is eqn. (2)[5] where the subscript + denotes the cation and the transport number t_+ is defined by eqn. (2a).

$$J_+A = t_+\frac{I}{F} + \dot{V}^o \cdot \frac{c_+^\alpha - c_+^\beta \exp\left(-\dfrac{\dot{V}^c l}{AD_\pm}\right)}{1 - \exp\left(-\dfrac{\dot{V}^c l}{AD_\pm}\right)} \quad (2)$$

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \quad (2a)$$

The diffusion coefficient D_+ for the salt is given by eqn. (2b) where λ_+ and λ_- are the equivalent conductivities of the cation and anion, respectively and I is the electric current.

$$D_\pm = \frac{2\lambda_+\lambda_-}{(\lambda_+ + \lambda_-)F^2}RT \quad (2b)$$

It is convenient to define dimensionless convection by

$$v^c = \frac{\dot{V}^c l}{AD_\pm} \cdot \quad (3)$$

Using eqns. (1) and (2), the mass balance can now be written as eqn. (4); eqn. (5) is an ordinary linear differential equation which can be easily solved (see below).

$$\frac{dc_+^\alpha}{dt} + \frac{c_+^\alpha}{V^\alpha}\left(\dot{V}^\alpha + \frac{\dot{V}^c}{1-\exp(-v^c)}\right) = \frac{\dot{V}^c}{V^\alpha}c_+^o - t_+\frac{I}{V^\alpha F} + \frac{\dot{V}^c}{V^\alpha}\frac{c_+^\beta \exp(-v^c)}{1-\exp(-v^c)} \quad (4)$$

$$c_+^\alpha = \frac{c_+\dot{V}^o - [c_+^o\dot{V}^o - c_+^\beta\dot{V}^c]\exp(-v^c) - t_+I(1-\exp(-v^c))/F}{\dot{V}^o - \dot{V}^\alpha\exp(-v^c)}$$

$$+ \left\{c_+^\beta - \frac{c_+\dot{V}^o - [c_+^o\dot{V}^o - c_+^\beta\dot{V}^c]\exp(-v^c) - t_+I(1-\exp(-v^c))/F}{\dot{V}^o - \dot{V}^\alpha\exp(-v^c)}\right\}\exp\left[-\frac{t}{V^\alpha}(\dot{V}^\alpha + \dot{V}^c/(1-\exp(-v^c)))\right] \quad (5)$$

Considering eqn. (5), we can deduce that the time needed to reach a steady state depends on the volume of the compartment V^α, and the convection, V^c; the greater the convection the faster the steady state is reached. When c_+^o, V^α, and I are set equal to zero, the same result as derived earlier by Rastas et al.[7] is obtained.

We want to point out that in a ternary electrolyte system, the solution of eqn. (1) is more problematic than in the binary case, since the transport problem modelled by the Nernst-Planck equations cannot be solved in closed form.[8,9,10] A numerical solution is however obtainable by discretizing eqn. (1) with respect to time assuming that J_i is constant in each time interval (t_o). Then, the solution of eqn. (1) is eqn. (6) where the times t_{K+1} and t_K denote $(K+1)t^o$ and Kt_o, respectively. It should be noted that the parameters I, λ_i, V^c, and c_i^β are implicitly included in the fluxes J_1 and J_2.

$$
\begin{aligned}
c_i^\alpha(t_{K+1}) = {} & c_i^\alpha(t_K) \exp\left(-\frac{V^\alpha}{V^\alpha} t_o\right) \\
& - \frac{J_i(t_K)A}{V^\alpha}\left(1 + \exp\left(-\frac{V^\alpha}{V^\alpha} t_o\right)\right) \\
& + \frac{V^o}{V^\alpha} c_i^o\left(1 + \exp\left(-\frac{V^\alpha}{V^\alpha} t_o\right)\right); \quad i = 1,2.
\end{aligned}
\tag{6}
$$

Until now we have assumed that the fluxes are stationary in the membrane, but if the porous *membrane is thick enough*, this assumption fails and the flux in eqn. (1) must be calculated from eqn. (7) where $w^c = V^c/A$.

$$
J_+ = -D_\pm \left.\frac{dc_+}{dx}\right|_{x=0} + t_+ \frac{I}{AF} + c_+ w^c
\tag{7}
$$

$$
\frac{\partial c_+}{\partial t} = D_\pm \frac{\partial^2 c_+}{\partial x^2} - w^c \frac{\partial c_+}{\partial x}
\tag{8}
$$

$$
c_+(x,0) = c^\beta; \quad 0 \leq x \leq l
\tag{8a}
$$

$$
c_+(0,t) = c^\alpha; \quad t > 0
\tag{8b}
$$

$$
c_+(l,t) = c^\beta; \quad t > 0
\tag{8c}
$$

Eqn. (7) is valid for the binary electrolyte case. The concentration gradient $dc_+/dx|x = 0$ refers to the limiting value on the boundary of the α side of the membrane. According to the Nernst-

Planck equations, both $D_\pm$ and $t_\pm$ are independent of concentration (cf. eqns. (2a) and (2b)). When the divergence of the equation corresponding to eqn. (7) within the membrane is taken (i.e. without the limiting value when $x \to 0$) eqn. (8) is obtained where we have assumed that the liquid is incompressible (div $w^c = 0$). To obtain $c = c(x,t)$ we have to use properly chosen boundary and initial values where c^α and c^β are constant and l is the membrane thickness. Eqn. (8) can now be solved, e.g., by using the Laplace transformation. The solution in Laplace plane is shown by eqn. (9) where $\bar{c}(x,s)$ is L-transformed concentration and s is the Laplace variable. The dependence of concentration on time can be obtained by the inverse Laplace transformation. Since the function to be transformed is meromorphic, the transformation can be done by searching the poles, which in this case are simple, and by applying Heaviside's expansion theorem. Thus, we have eqn. (10).

$$
\begin{aligned}
\bar{c}(x,s) = {} & \frac{c^\beta}{s} - (c^\beta - c^\alpha)\exp\left(\frac{w^c}{2D_\pm} x\right) \cdot \\
& \frac{1}{s} \frac{\sinh[((w^c)^2/4D_\pm + s/D_\pm)^{1/2}(l-x)]}{\sinh[((w^c)^2/4D_\pm + s/D_\pm)^{1/2}l]}
\end{aligned}
\tag{9}
$$

$$
\begin{aligned}
c(x,t) = {} & c^\beta - (c^\beta - c^\alpha)\exp\left(\frac{w^c}{2D_\pm} x\right) \cdot \\
& \frac{\sinh\left(\dfrac{w^c}{2D_\pm}(l-x)\right)}{\sinh\left(\dfrac{w^c}{2D_\pm}l\right)} \\
& + \sum_{k=1}^{\infty} \frac{2k\pi D_\pm \sin(k\pi(l-x)/l)}{(-1)^k\left(\dfrac{w^c}{4D_+} + \dfrac{k^2\pi^2 D_\pm}{l^2}\right)} \cdot \\
& \exp\left[-\left(\frac{w^{c2}}{4D_\pm} + \frac{k_\pi^2 D_\pm}{l^2}\right)t\right]
\end{aligned}
\tag{10}
$$

Eqn. (10) can now be used to solve J_+ according to eqn. (7) and the result obtained then substituted into eqn. (1) to give the transient behaviour in the case of a *thick* membrane. The procedure is straightforward but gives a com-

plicated result. This result is not presented here because the most important deductions can be made by considering eqn. (10): the exponent $(w^{c2}/4D_{\pm} + k^2\pi D_{\pm}/l_2)$ determines the time required to reach stationary flux assuming that the volume of compartment α is large enough to maintain a constant boundary concentration during this time. As can be seen, the increase of the convection w^c rapidly decreases the time needed for reaching stationary fluxes (note square of w^c). The second term, $k^2\pi D_+/l^2$, is related to pure diffusion and increases rapidly with larger k. The above behaviour of the serial terms leads to the necessity of taking only a few terms into account in the solution. Furthermore, the higher the convection the faster stationary flux is reached. In practice, only the first term, $(w^c)^2/4D_{\pm} + \pi D_{\pm}/l^2$, needs to be considered in order to get an idea of how rapidly stationary flux is attained. After stationary flux has been reached, the same procedure as used for the *thin* membrane can be utilized provided that V^{α} is large enough. If this is not the case, eqn. (1) with eqns. (7) and (10) has to be used.

References

1. Kontturi, K., Forssell, P. and Ekman, A. *Sep. Sci. Technol. 17* (1982) 1195.
2. Forssell, P. and Kontturi, K. *Sep. Sci. Technol. 18* (1983) 205.
3. Ekman, A., Forssell, P., Kontturi, K. and Sundholm, G. *J. Membr. Sci. 11* (1982) 65.
4. Kontturi, K., Ojala, T. and Forssell, P. *J. Chem. Soc. Faraday Trans. 1, 80* (1984) 3379.
5. Kontturi, K. *Sep. Sci. Technol. In press.*
6. Kontturi, K. and Pajari, H. *To be published.*
7. Rastas, J., Ekman, A. and Salminen, S. *Nature 211* (1966) 1132.
8. Sipilä, A. H., Ekman, A. and Kontturi, K. *Finn. Chem. Lett.* (1979) 97.
9. Taskinen, P. and Kontturi, K. *Finn. Chem. Lett.* (1980) 97.
10. Kontturi, K. and Sipilä, A. H. *Finn. Chem. Lett.* (1983) 1.