

Calculations of the limiting current density and the transition time

The electro dialysis cell (1) design (in particular, the special input and output devices of the solution) provide a laminar flow of the solution in the intermembrane space [63]. The laminarity of the hydraulic regime was proved by using CFD simulations and by comparing the experimental limiting current density with the value calculated using the L ev eque equation, which was deduced under the assumption of laminar flow in the intermembrane space [63].

The theoretical limiting current density, $i_{\text{lim}}^{\text{th}}$, which is achieved in the absence of coupled effects of concentration polarization (such as electroconvection, gravitational convection, and water splitting) can be calculated by the L ev eque equation [53]:

$$i_{\text{lim}}^{\text{th}} = \frac{FDz_1C_1}{h(T_1 - t_1)} \left[\left(1.47 \frac{h^2V}{LD} \right)^{1/3} - 0.2 \right] \quad (1)$$

where F is the Faraday constant; D is the electrolyte diffusion coefficient; z_1 and C_1 are the charge and the input molar concentration of the counterion; T_1 and t_1 are the effective transport number of the counterion (Cl^- in the considered cases) in the membrane and its transport number in solution; V is the average linear flow velocity; L is the length of the desalination path; h is the intermembrane distance.

The parameters used in the experiments (at 20  C) are as follows: $D=1.425 \cdot 10^{-9} \text{ m}^2/\text{s}$, T_1 is assumed to be 1, t_1 is 0.605, V is $0.38 \text{ cm} \cdot \text{s}^{-1}$, h is 6.5 mm, and L is 2 cm. The value calculated from Eq. (1) for these experimental conditions is $2.8 \text{ mA} \cdot \text{cm}^{-2}$.

The limiting current density $i_{\text{lim}}^{\text{th}}$ is related to the diffusion layer effective thickness, δ , by the Peers equation [64]:

$$i_{\text{lim}}^{\text{th}} = \frac{FDz_1C_1}{\delta(T_1 - t_1)} \quad (2)$$

A combination of Eqs. (1) and (2) gives δ equal to 250  m.

To compare chronopotentiograms of different membrane systems, it is convenient to use the reduced potential drop $\Delta\varphi'$ [54] instead of the total potential drop, $\Delta\varphi$:

$$\Delta\varphi' = \Delta\varphi - \Delta\varphi_{ohm} \quad (3)$$

where the ohmic potential drop, $\Delta\varphi_{ohm}$, of the unpolarized membrane system is found by the extrapolation in the $\Delta\varphi - \sqrt{t}$ coordinates to zero time (the time of the current switch-on).

The theoretical transition time, τ_{Sand} , is found using the Sand equation [49]:

$$\tau_{Sand} = \frac{\pi D}{4} \left(\frac{Fz_1 C_1}{T_1 - t_1} \right)^2 \frac{1}{i^2} \quad (4)$$

Eq. (4) allows estimating the transition time in the case where the membrane surface is homogeneous and smooth, and electrolyte transfer is governed only by electro-diffusion.

The experimental current-voltage curves are plotted in the coordinates of the ratio of the current density to its theoretical limiting value i/i_{lim}^{th} versus the reduced potential drop $\Delta\varphi'$. In this case $\Delta\varphi'$ is related to the measured potential drop as

$$\Delta\varphi' = \Delta\varphi - iR_{i=0} \quad (5)$$

where $\Delta\varphi$ is the measured value of potential drop at a current density i and $R_{i=0} = \left(\frac{\partial\Delta\varphi}{\partial i} \right)_{i \rightarrow 0}$ is the resistance of the membrane system at $i \rightarrow 0$.