CHRONOPOTENTIOMETRIC CHARACTERIZATION OF ELECTRODIALYSIS MODULE

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Abstract

Classical and chronopotentiometric characterization of the electrodialysis module at the same concentrations of diluate and concentrate was performed. Limiting current was determined from the Cowan-Brown plot, the current efficiency and the mean transport number of counterions – from the concentration changes on the exit of the ED module. The electric resistance was determined from the chronopotentiometric curve. For electric currents higher than the limiting one, the transition time (inflection point) was observed. Thus, having such curves for different values of electric current, the limiting current can be roughly estimated. To estimate a mean counterion transport number from the transition time, an equation, analogous to the Sand equation, should be developed which include both types of membrane.

Streszczenie

Przedstawiono krzywe chronopotencjometryczne elektrodialitycznego modułu membranowego, Stwierdzono, że na ich podstawie można określić, czy zastosowane natężenie prądu nie przekracza prądu granicznego, a tym samym w przybliżeniu określić wartość tego ostatniego. Oszacowana na podstawie kilku krzywych chronopotencjo-metrycznych wartość prądu granicznego jest zgodna z wyznaczoną wartością na podstawie wykresu Cowana-Browna. Obserwowane na krzywych punkty przegięcia można wykorzystać do wyznaczenia średniej liczby przenoszenia przeciwjonów. W tym celu należy wyprowadzić równanie analogiczne do wzoru Sanda, które by brało pod uwagę oba rodzaje membran w module. Ponadto, krzywe chronopotencjometryczne pozwoliły na proste i szybkie wyznaczenie oporu elektrycznego modułu.

Keywords: **Electrodialysis; Chronopotentiometry; Limiting current; Current efficiency.**

1. INTRODUCTION

Electrodialysis (ED) is a membrane process driven by the electric force which found application in many different areas [1, 2]. The main characteristics of the membrane stack used in the ED system, working in given conditions (electrolyte, concentration, flow velocity, etc.) include the limiting current, current efficiency, module electric resistance, which determine energy efficiency of the process.

Chronopotentiometry is an electrochemical technique which for ion-exchange membranes was applied for the first time probably by Block and Kitchener [3], later by Brennen and Hills [4], and other authors, e.g. [5-8]. It can be used for the determination of ion transport numbers in a single membrane [9] and of the system resistance [10]. Extensive chronopotentiometric studies of a cation-exchange membrane in a module for reverse electrodialysis were published by Pawlowski et al. [11].

In this work we investigate chronopotentiometrically the whole ED module containing 18 membrane pairs. Comparing to a single membrane system where the experimental conditions are well defined, the ED

module contains two types of ion-exchange membranes which can differ in the degree of concentration polarization at their surfaces. Moreover, the concentration of solutions along their path in the ED module is not uniform [12]. Thus we may expect that the limiting current, I_{lim}, covers a certain range of values and the transition time observed for a single membrane in the overlimiting current range for the ED stack may not be clearly seen. The aim of this paper is to verify whether the transition time can be observed for values of electric current above and close to I_{lim} determined by the classical method from the Cowan-Brown plot [13, 14]. If yes, then the chronopotentiometric curves would allow for a rough estimation of I_{lim} and to check if the ED module works in the under- or overlimiting current range. Additionally the resistance of the ED stack has been determined.

2. EXPERIMENTAL

The laboratory batch ED setup (Aqualyzer® Corning) equipped with 18 pairs of the PC-SA and PC-SK membranes (PCA GmbH) was used. In the membrane stack the flows of diluate and concentrate were perpendicular to each other. The active area of a single membrane was 70.6 cm². The dilute and concentrate circuits were connected to a common tank containing 0.017 M Na$_2$SO$_4$. The volume flow of solutions through the module was 50 L/h, the thickness of spacers was 0.4 mm. The electrode solution was ca. 0.3 M Na$_2$SO$_4$. The conductance and temperature on the exit of diluate from the membrane module were measured. From these data the concentration was calculated using the formula as in [15].

Cowan-Brown plot. At the constant voltage the electric current and conductance of diluate on the module exit were measured until they were constant. The experiment was repeated for various values of voltage covering the appropriate range of the electric current.

Chronopotentiometric measurements. The voltage drop on the membrane stack was measured using two platinum wires placed on both sides of the membrane stack. The time interval of data logging was 0.5 s (multimeter KEITHLEY 2700).

The data shown in Fig. 1 were obtained in a four compartment membrane stack, where the investigated membrane was separated from the electrode chambers with two auxiliary membranes.

3. RESULTS AND DISCUSSION

3.1. Limiting current and current efficiency

Before chronopotentiometric experiments, the limiting current for the ED module was determined from the Cowan-Brown plot (Fig. 1). Approximating the region near $(U/I)_{min}$ with e.g. polynomial it was found that $I_{lim} = I_{min} = 0.57$ A.

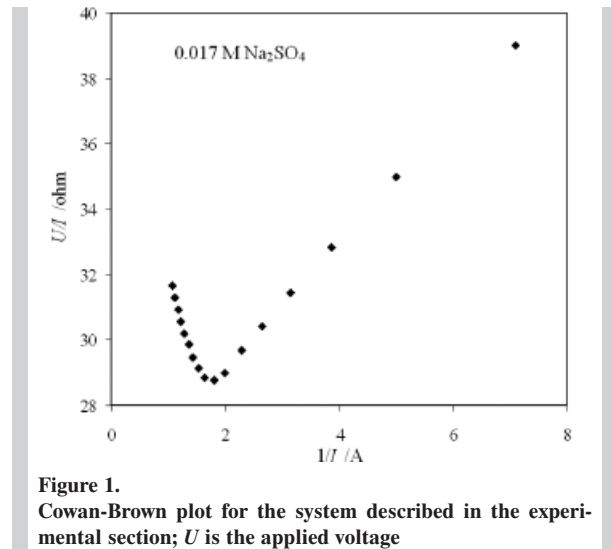**Figure 1.**
Cowan-Brown plot for the system described in the experimental section; U is the applied voltage

The current efficiency, CE, was calculated from the diluate concentrations determined during the measurements $I = f(U)$ (Fig. 2) using the formula:

$$CE = \frac{F\dot{V}}{n_{cd}}\frac{dc_{dil}}{dI} \qquad (1)$$

where n_{cd} is number of compartment pairs, $\dot{V}$ is volume flow of diluate solution. Although it seems that all the points are roughly on the same straight line, we approximated $c_{dil}(I)$ in two ranges – for $I < I_{lim}$ and $I > I_{lim}$ which gives slopes dc_{dil}/dI equal 0.0056, 0.0050 mol·dm^{-3}A^{-1}, respectively. It indicates that above I_{lim} the current efficiency decreases, in this case ca. 10%. The obtained values $CE = 0.83$ and 0.74 are low considering the fact that the bulk concentration of Na$_2$SO$_4$ was not excessively high. Because of a small concentration, the diffusional contribution to CE is small and CE can be regarded as a function of ion transport numbers only: $CE \approx \bar{t}_{+,CM} + \bar{t}_{-,AM} - 1$ [16], where $\bar{t}_{+,CM}, \bar{t}_{-,AM}$ are the counterion transport numbers in cation- and anion-exchange membranes. Thus, the average transport number of Na$^+$ and SO$_4^{-2}$, $(\bar{t}_{+,CM} + \bar{t}_{-,AM})/2 \approx (1 + CE)/2$, is equal 0.92 ($I < I_{lim}$) and 0.87 ($I > I_{lim}$).
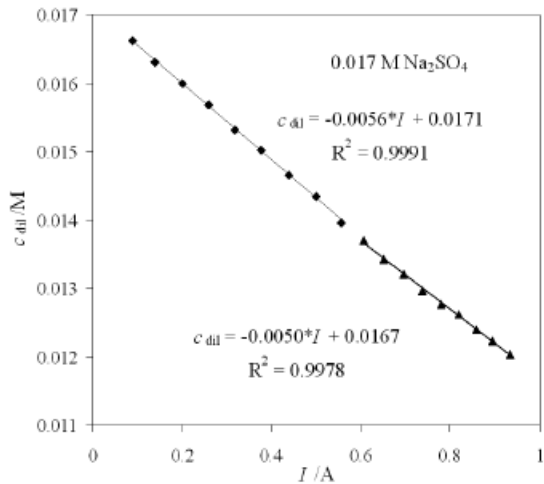
Figure 2.
Diluate concentration at the ED module exit versus electric current during the $I(U)$ measurements

$c_{dil} = -0.0056*I + 0.0171$
$R^2 = 0.9991$

$c_{dil} = -0.0050*I + 0.0167$
$R^2 = 0.9978$

0.017 M Na$_2$SO$_4$

Figure 3.
Exemplary chronopotentiometric curve measured for the Nafion 120 membrane in 0.1 M NaCl ($I > I_{lim}$); vertical membrane position, no flow along the membrane surface; the differential quotient $\Delta V/\Delta t$ shows more clearly the transition time τ; the parts of curve – a, b, c – are described in the text; for better readability the data can be smoothed by an appropriate method

$\tau = t_{IP} - t_0$

Nafion 120 - 0.1 M NaCl

3.2. Chronopotentiometric curves

To show the differences between single membrane and the ED stack the chronopotentiometric curve for a single membrane without solution stirring was also performed. Three main parts of such curve are clearly seen (Fig. 3): "a" corresponds to a sudden ohmic increase in voltage immediately after a fixed current was applied, "b" – here the concentration in the polarization layer decreases until its value at the membrane surface reaches zero (the transition time τ). Assuming that the thickness of boundary diffusion layer goes to infinity, the transition time is given by the Sand equation (Eq. (16) in [4]):

$$\tau = \frac{\pi D_s}{4}\left(\frac{z_1 c_{1,0} F}{(\bar{t}_1 - t_1)j}\right)^2 \qquad (2)$$

where j is current density, F – Faraday constant, D_s – diffusion coefficient of electrolyte, z_1, $c_{1,0}$, t_1 – charge number, bulk concentration, transport number in the solution (at the membrane surface) of ion 1, respectively. Having determined τ, the transport number of ion "1" in the membrane, $\bar{t}_1$ can be estimated. In the case of finite thickness of polarization layer, there is no analytical solution and the continuity equation should be solved numerically.
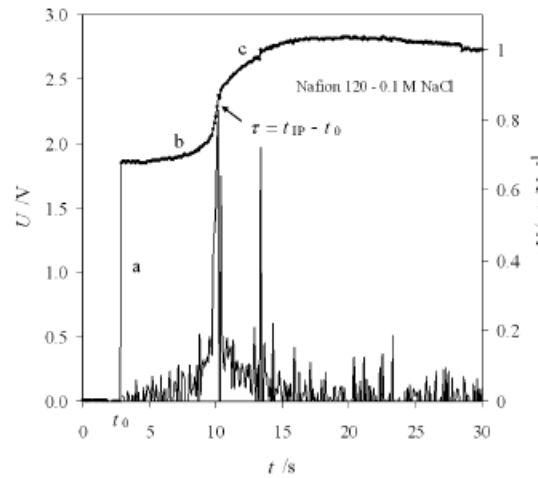
Taking into account that the obtained earlier limiting current value is 0.57 A, we decided to determine the chronopotentiometric curves for the following values of I: 0.5, 0.55, 0.6 and 0.65 A (Fig. 4). Comparing Fig. 4 with Fig. 3 it is seen that in the case of the ED module it is more difficult to localize the inflection point. The reasons of not so clear shape of curve are: 1) flowing solutions along the membrane surface reduce the polarization layer thickness, 2) in the compartments, diluate (and concentrate) concentration changes along the solution flow path [12], 3) there are two different types of membranes. Thus, I_{lim}, which depends on these effects, should not be uniform. Analyzing the plots of the differential quotient $\Delta V/\Delta t$ one can notice maxima for $I = 0.6$ and 0.65 A, whereas for $I = 0.5$ and 0.55 A such maxima are not visible. It leads to the conclusion that the limiting current is within the range 0.55-0.6 A. It is in accordance with $I_{lim} = 0.57$ A obtained from the Cowan-Brown plot. The position of two maxima are $\tau_1 = 9.5$ and $\tau_2 = 11$ s for $I = 0.60$ and 0.65 A, respectively. These data fulfill the condition $I\tau_1^{1/2} = I\tau_2^{1/2}$ ($I\tau_1^{1/2}/(I\tau_2^{1/2}) = 1.007$) which should be fulfilled for a single membrane according to the Sand equation (1). However, more experimental points are needed to confirm (or reject) this observation.
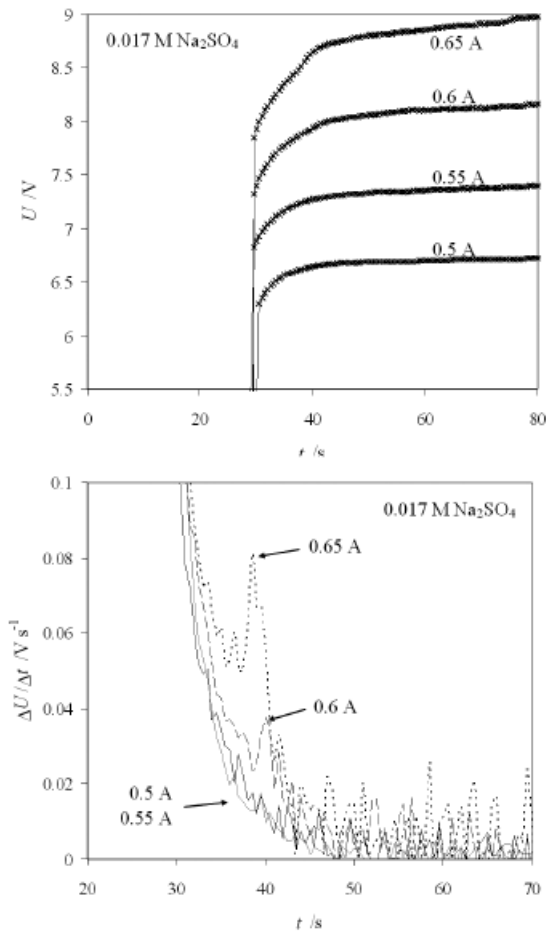
Figure 4.
Top: chronopotentiometric curve for the ED module described in the text; bottom: $\Delta V/\Delta t$ of that curve

Unfortunately, it is not possible to apply the simple Sand equation to evaluate a mean transport number of counterions. Firstly, it was derived for infinite thickness of boundary diffusion layer. We have checked that for our current density and Na_2SO_4 concentration, the thickness calculated from the solution of continuity equation under that assumption (eq.(14) in [4]) would be 0.22 mm (at 5% decrease in the bulk concentration) – too much regarding the spacer thickness equal 0.4 mm. Secondly, there are two kinds of membranes, although the case where the electric current is limited mainly by one kind can be considered. To dispel any doubts we calculated $\bar{t}_1$ from eq.(2) assuming that I_{lim} is determined by the polarization layer predominantly at 1) cation-, 2) anion-exchange membranes. In the first case $\bar{t}_+$ was ca. 0.73, in the 2nd case $\bar{t}_-$ was 0.96. The mean counterion transport number obtained from the concentration changes (0.92-0.87, see above) is within

these values. However, because of large discrepancies a new model should be developed which connects the transition time observed for the ED module with the transport numbers of counterions in the membranes constituting that module.

From the sudden increase in voltage (part "a" of chronopotentiometric curve) the resistance of the membrane stack ($R = \Delta U/I$) was determined. For $I = 0.5, 0.55, 0.6, 0.65$ A we obtained the following values: 12.2, 12.1, 12.0, 12.0 Ω. A slight decrease in resistance with I is observed. Again, more measurements in a wider range of I are needed to judge if it is a regularity or just an experimental error.

4. FINAL REMARKS

The chronopotentiometric method in relation to ion-exchange membranes supplies important information, is fast, and does not need a sophisticated instrumentation. From chronopotentiometric curves the resistance of ED module is readily accessible. Using them one can check if the ED process runs at the under- or over-limiting current regime. It is also possible to determine approximately the limiting current, however not so directly as from the Cowan-Brown plot. The transition time, observed for electric currents higher than the limiting one, can be applied for the determination of the mean transport number of counterions. However, for that purpose an adequate theory should be developed; the Sand equation is not appropriate here.

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