Mass transfer in reverse electrodialysis: Flow entrance effects and diffusion boundary layer thickness

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A B S T R A C T

Power generation by reverse electrodialysis (RED) depends on ionic mass transfer through alternately arranged cation- and anion-exchange membranes. Chronopotentiometric measurements were carried out in an EDR-Z Mini stack (MEGA a.s.), equipped with Ralex heterogeneous membranes, separated by either sheet flow spacers or mesh-free gaskets. Various concentrations of model NaCl solutions were used to study the ohmic and non-ohmic resistances in the stack under different hydrodynamic conditions. In order to eliminate the uncertainties associated with a non-uniform distribution of the applied current over the membrane surface, the relaxation zone of the obtained chronopotentiograms was used to estimate the diffusion boundary layer thickness. It was found that this approach provide more accurate data under RED operating conditions, which are strongly influenced by entrance effects on mass transfer, especially for a spacer-free channel configuration. For shorter flow channels, since the salt concentration profile across the diffusion boundary layer is not yet fully developed, more power can be obtained than in the case of longer channels. The presence of spacers was found to reduce the boundary layer thickness, but also increased the ohmic resistance, due to their shadow effect over the membrane surface. The description of the impact of flow entrance effects on mass transfer, and therefore on diffusion boundary layer thickness, can be useful for characterization and further design and/or optimization of RED stacks performance.

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1. Introduction

Reverse electrodialysis (RED) is one of the emerging sustainable technologies for renewable power generation, which is based on harvesting salinity gradient energy [1–4], released when two aqueous streams of different salinity are mixed. In a RED stack, composed by alternately-arranged cation- and anion-exchange membranes, stacked between two electrodes, the chemical energy associated with solvation of salts can be directly converted into electrical energy. The global theoretically obtainable power from salinity gradient energy due to World's rivers discharge into the oceans has been estimated to be within the range of 1.4–2.6 TW [4, 5].

The power output of a RED stack depends on its internal resistance (ohmic and non-ohmic) and on the total potential difference established between the electrodes [6–11]. The main ohmic resistance is commonly located in the compartments of the dilute (salinity usually below 0.1 M NaCl) stream [12–14]. This resistance can be reduced by decreasing the intermembrane distance [2,6,15–17]; however, in such situations, most probably

due to small changes in the spacers structure, an increase of concentration polarization (non-ohmic resistance) in the diffusion boundary layers (DBLs) adjacent to the membranes forming the stack compartments [2,6,16–17] has been reported. In result, at a sufficiently low linear fluid flow velocity, the total resistance in a narrow stack compartment has become even higher than that in a thicker one [17]. Also, as a consequence of concentration polarization, the potential difference established between the electrodes drops, since the salt concentration gradient across the membranes becomes lower [7,17].

Promoting fluid mixing, through an increase in the linear flow velocity and/or introducing spacers, can reduce the thickness of the diffusion boundary layer (DBL) [6,11,13,14,17,18]. However, in both cases, this also increases the pressure drop, which negatively affects the obtainable net power density [6,11,12,19,20]. Furthermore, the "shadow" effect imposed over the membranes by non-conductive spacers tends to additionally reduce the ionic mass transport and increase the ohmic resistance [11,12,17,21].

In systems with ion-exchange membranes, the chronopotentiometry has been proven to be a very useful tool to perform the process analysis, since it allows for a direct access of the voltage contributions in polarized and non-polarized solution-membrane systems [22–24]. The respective electrochemical measurements

are usually performed in dedicated lab-scale cells with electrodes (normally Haber–Luggin capillaries) located close to the two sides of a very small ion-exchange membrane area available for counter-ion transport [23–28]. The electrolyte solutions on both sides of the membrane are usually dilute in order to guarantee an efficient Donnan exclusion of the co-ions and therefore preferential transport of counter-ions in the membrane [23,25,29]. Moreover, in a RED stack the salt concentration profile within the DBL gradually develops from the channels entrance to a certain channel length before becoming fully developed [30,31]. Therefore, only an approximate agreement could be expected between data obtained in dedicated electrochemical cells and in an operating RED stack.

There are experimental evidences that the obtainable power density in shorter channels is higher than in longer channels, as the measured non-ohmic resistance was lower in such cases [32]. However, the effect of decreasing the channels' length on the net power density had been only considered in terms of lower pressure drop and/or smaller decrease in potential difference, due to solutions mixing, along the channel [8,33–35]. The possible impact on power generation of flow entrance effects, which extend to a longer channel length as the fluid linear flow velocity increases [30, 31], has not yet been reported. The models [8–9,19,33] which have so far been proposed to simulate and/or predict the performance of a RED stack either do not consider concentration polarization effects [19,33], or the non-ohmic resistance has been estimated by an empirical equation obtained under the studied conditions [8], or it has been considered that the resistance is dependent from a previously assumed DBL thickness value [9].

In this study, different methodologies were tested and compared in order to allow for more accurate DBL thickness estimation in a RED stack. Utilization of diffusion relaxation chronopotentiometry data is proposed for the first time in order to access the diffusion boundary layer thickness under RED operating hydrodynamic conditions. It has been found that this approach is the most accurate one within the linear flow velocity range relevant for RED, if the estimations are based on electric potential values. Also, a comparison of experimental results with the Leveque equation predictions for spacer-free channels was performed in order to allow for evaluating the impact of flow entrance effects on mass transfer. Finally, the influence of the streams' salinity on the ohmic and non-ohmic stack resistances was evaluated.

2. Theory

2.1. Linear sweep voltammetry

The DBL thickness (δ) is usually calculated from experimental data of the limiting current density (i_{lim}) obtained for a cation-exchange membrane by linear sweep voltammetry [23,25–27,29,36,37]

$$i_{lim} = \frac{z_+ DFC_b}{(T_+ - t_+)\delta},\qquad(1)$$

where F is the Faraday constant and z_+, T_+, and t_+ are respectively the cation valence, effective transport number in the membrane and transport number in the solution, with known salt diffusivity (D) for a given salt concentration in the bulk (C_b).

For relatively short ($L < 0.02u\,h^2/D$) rectangular channels without mixing promoters and, therefore, under conditions of a not fully developed salt concentration profile across the DBL [30], the limiting current density can be estimated by the Leveque

equation [25–27,29,37–39]

$$i_{lim} = \frac{1.47FDC_b}{h(T_+ - t_+)}\left(\frac{h^2u}{LD}\right)^{1/3},\qquad(2)$$

where u is the fluid linear flow velocity inside a channel with a known length (L) and intermembrane distance (h). The Leveque equation considers the existence of electroconvection, which may be suppressed in case of competitive transfer through the membrane of H^+/OH^- ions, as they carry the charge without bringing any liquid volume into motion [27,37,40]. This is a semi-empirical correlation which, for the case of natural convection, is compatible with Levich-kind of equations based on the physical deduction for a channel formed between two plane parallel electrodes, in which a steady state laminar solution flow is established [28].

The limiting current density, and therefore the DBL thickness, can be also estimated by empirical correlations. In such cases, the working flow channel geometry, the fluid properties, as well as the hydrodynamic conditions are considered. When mixing promoters are present, correlations in the form of $Sh = aRe^bSc^c$ are widely used [41,42].

The Sherwood number (Sh) is correlated with the Reynolds number (Re), which depends on the hydrodynamic conditions and the channel hydraulic diameter (d_{ch}). The value of the exponent of the Reynolds number is usually 0.33 for a laminar regime, 0.5 if mixing promoters are present and 0.7–1.0 for a fully developed turbulent regime [42]. The Schmidt number (Sc) exponent is commonly set as 0.33 [31,41–44]. For a bench-scale ED stack, with a geometry similar to that of the investigated RED stack, the proposed correlation is [43]

$$Sh = 0.29Re^{0.5}Sc^{0.33}.\qquad(3)$$

Since the Sherwood number (Sh) depends on the mass transfer coefficient ($k = D/\delta$)

$$Sh = \frac{kd_{ch}}{D},\qquad(4)$$

and the limiting current density also depends on the ratio D/δ (Eq. (1)), its estimation becomes possible by using the Sherwood number

$$i_{lim} = \frac{z_+ FC_b}{(T_+ - t_+)}\frac{ShD}{d_{ch}},\qquad(5)$$

where the channel hydraulic diameter for channels with spacers is [8]

$$d_{ch} = \frac{4\varepsilon}{\frac{2}{h} + (1-\varepsilon)\frac{S_{sp}}{V_{sp}}},\qquad(6)$$

where ε is the spacer porosity from the flow direction perspective and S_{sp}/V_{sp} is the ratio of the surface to volume of the spacer filaments.

2.2. Chronopotentiometry

To calculate the DBL thickness within the under-limiting current density range, chronopotentiometric measurements could be performed as illustrated in Fig. 1.

A unidimensional counter-ion transport, described through the Nernst–Planck formalism within the two DBLs adjacent to the membrane, is considered in a system composed by a single cation-exchange membrane that separates two 1:1 electrolyte (e.g. NaCl) solutions. The following equations can be written for the resulting electric potential drops in the steady state, if co-ion transport is neglected and the electrolyte concentration is the same on both