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# Membrane resistance: The effect of salinity gradients over a cation exchange membrane

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## ABSTRACT

Ion exchange membranes (IEMs) are used for selective transport of ions between two solutions. These solutions are often different in concentration or composition. The membrane resistance ( $R_M$ ) is an important parameter affecting power consumption or power production in electro-dialytic processes. In contrast to real applications, often  $R_M$  is determined while using a standard 0.5 M NaCl external solution. It is known that  $R_M$  increases with decreasing concentration. However, the detailed effect of a salinity gradient present over an IEM on  $R_M$  was not known, and is studied here using alternating and direct current. NaCl solution concentrations varied from 0.01 to 1.1 M. The results show that  $R_M$  is mainly determined by the lowest external concentration.  $R_M$  can be considered as two resistors in series i.e. a gel phase (concentration independent) and an ionic solution phase (concentration dependent). The membrane conductivity is limited by the conductivity of the ionic solution when the external concentration,  $c_{ext} < 0.3$  M. The membrane conductivity is limited by the conductivity of the gel phase when  $c_{ext} \geq 0.3$  M, then differences of  $R_M$  are small. A good approximation of experimentally determined  $R_M$  can be obtained. The internal ion concentration profile is a key factor in modeling  $R_M$ .

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## 1. Introduction

Ion exchange membranes are widely used for concentrating and/or selective transport of dissolved charged particles, for example in electro-dialysis (ED) for desalination purposes [1–3]. Although ED is in practice most used for brackish water desalination, it recently gained interest as a seawater (pre) desalination technology [4,5]. In addition, an electro-dialysis stack can be used for the production of salinity gradient energy in the opposite process i.e. reversed electro-dialysis (RED), by mixing river water and seawater [6–9]. The salt concentrations of the solutions in a RED stack are comparable to those in a seawater ED stack. In the ED process low energy consumption is desired and in RED high power production is targeted. In both situations low stack resistances are a prerequisite.

Generally, membrane resistances are determined at an external salt concentration of 0.5 M NaCl and a temperature of 25 °C. Literature shows that membrane resistance depends on the concentration of the external solution [10–16]. In practical applications of ED or RED, the

concentration at either side of the ion exchange membrane differs. It is, however, unknown how this determines the membrane resistance. Recent research indicated that the membrane resistance is significantly higher compared to high salinities at both sides of the membrane when a solution low in salinity is present at one side of the membrane and liquid with a high salinity at the other side [16]. This previous research indicated that the actual membrane resistance in practical applications may be an order of magnitude higher than specified in standard resistance characterization measurements with 0.5 M solutions at both sides of the membranes.

Although the membrane resistance between external solutions of unequal concentration is particularly interesting for many practical applications, no systematic quantitative experimental research has been performed on this topic. Veerman et al. attempted to model the membrane resistance in cases with different salinity at both sides quantitatively [8]. To validate this model, and gain fundamental knowledge on membrane resistance in practical applications, this paper presents experimental results on the resistance of ion exchange membranes, having different salinities at both sides (0.01–1.1 M NaCl). This experimental data provides a solid fundament for a model, presented in this research, to estimate the (cat-) ion exchange membrane resistance, even

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when using different salt concentrations at either side of the membrane. This knowledge improves the modeling of processes in ED and RED [17,18] and furthermore provides insight in how to influence the membrane resistance for practical applications.

## 2. Theory

Determination of the ‘membrane resistance’ is not straightforward as the measurement is influenced by changes in the membrane environment. Długołęcki et al. [11,12] investigated single membranes at several NaCl concentrations (range 0.017–0.5 M) and distinguished the ohmic (true) membrane resistance ( $R_M$ ), the resistance of the electric double layer ( $R_{DL}$ ), and the resistance of the diffusional boundary layer ( $R_{DBL}$ ). Długołęcki et al. [11,12] showed that, at low external NaCl concentrations ( $< 0.1$  M), the diffusion boundary layer resistance ( $R_{DBL}$ ) is the main resistance, while at 0.5 M the true membrane resistance ( $R_M$ ) accounts for the largest part of the observed membrane resistance [11,12].

In the present article, the electric double layer resistance as defined in [12,19] is not included as a separate resistance, as there is no convincing evidence for it to be significant; the effect is considered here to be part of the diffusion boundary layer, which is further referred to as stagnant diffusion layer (SDL) [20,21]. Consequently the observed membrane resistance is given by the summation of the true membrane resistance and the resistance of the SDL:

$$R_{M+SDL} = R_M + R_{SDL} \quad (1)$$

Ion exchange membranes (IEMs) contain a fixed charge, which stems from the ion exchange groups covalently bound to the membrane polymer. For cation exchange membranes e.g. sulfonic acid groups are used, while for anion exchange membranes e.g. quaternary ammonium groups are used [1,2]. Ions with a charge opposite to the fixed membrane charge density,  $X$  (mol/m<sup>3</sup> of internal solution [22]) are called counterions, while ions with a charge similar to  $X$  are called co-ions. So for a cation exchange membrane Na<sup>+</sup> ions are the counterions and Cl<sup>-</sup> ions are the co-ions. The degree to which counterions can pass the membrane and the passage of co-ions is prevented, is reflected by the permselectivity ( $\psi^m$ ), which was defined by Winger et al. [23] as

$$\psi^m = \frac{T_{cou}^m - T_{co}^s}{T_{co}^s} \quad (2)$$

where,  $T_{cou}^m$ ,  $T_{co}^s$  and  $T_{co}^s$  are the transport numbers (dimensionless) of respectively the counterions in the membrane, the counterions in solution and the co-ions in solution. Assuming electro neutrality within the membrane, the fixed membrane charge density, the counterion concentration in the membrane ( $\bar{c}_{counterion}$ ) and the co-ion concentration in the membrane ( $\bar{c}_{co-ion}$ ) are related according to Eq. (3):

$$X + \bar{c}_{co-ion} = \bar{c}_{counterion} \quad (3)$$

The counterion concentration in excess to the membrane charge is referred to as ‘free ion concentration’ and is equal to the co-ion concentration, therefore  $\bar{c}_{co-ion} \equiv \bar{c}_{free}$ . These free ions could be of particular interest to model membrane conductance, as these ions are not associated with a fixed charge and depend on the external concentration [24]. Previously, the relation between the external NaCl concentration and the internal concentration was investigated [22]. This research concluded that the Boltzmann equation underlying the classical Donnan theory is valid to use for densely charged ion exchange membranes. In the original Boltzmann theory ions are regarded as point charges, in very narrow pores ( $\sim 1$  nm), ion size is no longer completely negligible. Therefore it is necessary to include a small (energetic) size exclusion

term ( $\mu^* = 0.2$  kT), leading to the relationship given by Eq. (4) [22]

$$\bar{c}_{counterion} + \bar{c}_{co-ion} = \sqrt{X^2 + (2c_{ext} \exp(-\mu^*))^2} \quad (4)$$

where,  $c_{ext}$  is the external salt concentration (mol/m<sup>3</sup>). The fixed membrane charge density,  $X$  is not a constant because it is expressed per unit volume and therefore changes with the swelling degree of the membrane according to Eq. (5) [22]:

$$X = X_0 \frac{w_0}{w} \quad (5)$$

where,  $X_0$  is the fixed membrane charge density estimated at an external NaCl solution concentration of zero ( $= 5.7$  M, in case of a Neosepta CMX membrane [22]),  $w_0$  is the accompanying CMX membrane water content (0.3113 g/g [22]), and  $w$  is the actual water content ( $= w_0 - 0.0167c_{ext}$  g/g [22]) of a CMX membrane at the given external solution concentration,  $c_{ext}$  (M).

By combining Eqs. (3) and (4), the equation to determine the co-ion (or free ion) concentration becomes

$$\bar{c}_{co-ion} = \frac{1}{2} \left( \sqrt{X^2 + (2c_{ext} \exp(-\mu^*))^2} - X \right) \quad (6)$$

Eq. (6) shows that, due to the Donnan equilibrium, a decrease in ion concentration of the external solution ( $c_{ext}$ ) leads to a decrease of the (free) ion concentration of the internal membrane solution [22,24–27]. If the ion concentration of a solution decreases, the conductivity of the solution decreases proportionally (and almost linear below 1.0 M). Resistance of a salt solution ( $R$ ,  $\Omega$ ) is related to the conductivity ( $\sigma$ , S/m) as shown in Eq. (7)

$$R = \frac{1}{G} = \frac{\delta}{\sigma A} = \frac{\delta}{\Lambda c A} \quad (7)$$

where,  $G$  is the conductance (S),  $A$  is the area (m<sup>2</sup>),  $\delta$  is the thickness (m),  $\sigma$  is the conductivity (S/m),  $\Lambda$  is the molar conductivity (S m<sup>2</sup>/mol), and  $c$  is the concentration (mol/m<sup>3</sup>). The conductivity of a material is defined by the concentrations and mobilities of the charge carriers it contains [25]. In ion exchange membranes, the charge is carried by ions. The mobility of these ions is expressed by their diffusion coefficient (related through the Einstein–Smoluchowski equation [28,29]). As described by Helfferich [25], a high membrane conductivity is favored by: (i) a high membrane charge density, (ii) low degree of cross-linking, (iii) small ion size, (iv) low ion valence, (v) high external solution concentration and (vi) elevated temperature.

The membrane resistance is only one part of the total ED/RED stack resistance. Additional resistance is created by electrodes and liquid phase. By adjusting the electrolyte system or the electrode coating, the overpotential (due to concentration polarization) and the electrode resistance can be minimized [8,30,31]. Channel thickness, and consequently liquid resistance, can also be optimized for the system. Membrane resistance especially becomes important for processes where electrode and flow channel resistances are minimized, or when the membrane resistance is relatively large compared to the other resistances, e.g. when very thin flow channels or profiled membranes are used [7,32].

NaCl concentrations of the external solutions, which are unequal at both sides of an ion exchange membrane result in a chemical potential gradient over the membrane. This induces ionic diffusion and osmotic water transport. In electrochemical systems such as ED and RED, water transport can take place due to osmosis (free water) or due to electro-osmosis (water transport together with the ion, as its hydration sphere) [1,2,33–35]. In electrodialysis, the osmotic and electro-osmotic water flux are in the same direction (towards the concentrate) and can have a large influence on the separation process [2,5,33,34,36]. For RED, water transport is of less influence as electro-osmosis and osmosis are in opposite

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