An integrative modeling and experimental study on the ionic resistance of ion-exchange membranes

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ARTICLE INFO

ABSTRACT

In many applications, the ionic resistance of an ion-exchange membrane shows a strong dependency on the external solution concentration and hydrodynamic environment. It is critical to understand the insights of ion exchange membrane process if its ionic resistance can be simulated accurately. In this paper, we have developed a new model by taking into account both the membrane properties that affect the membrane bulk resistance and hydrodynamic environment that affects the non-ohmic behavior of membrane resistance. The new model not only explains external solution concentration dependency, but also explicitly establishes a relationship between the measured membrane resistance and current density. The modeling results on the direct current (DC) and alternating current (AC) resistance of membranes are compared with experimental data measured under different external solution concentrations and applied current densities. We demonstrate that the model accurately predicts the behaviors of sulfonated polypoly (2,6-dimethyl-1,4-phenylene oxide) membranes and fumasep®-FKS and FAS membranes in all cases. The integrative modeling and experimental study provides insights into the ion-exchange membrane synthesis as well as reverse and conventional electrodialysis processes.

1. Introduction

Ion-exchange membranes are widely used in various electrochemical systems [1–6]. Key membrane properties, such as electrical resistance and permselectivity, usually maintain the functionality and determine the efficiency of these systems. The selectivity of ion-exchange membranes enables the separation of cations and anions in a solution thereby making electrodialysis and deionization processes possible. The efficiency of system operation depends on the overall electrical resistance of the system which is significantly determined by membrane resistance. For example, salinity gradient energy generated through reverse electrodialysis (RED), has been a hot topic for researchers who see ion-exchange membranes as the key component of RED conversion [7–9]. Membrane resistance is critical in this application since the output power density is directly affected by energy lost from electrical resistance.

The ionic resistance of an ion-exchange membrane is commonly determined by experimental methods using direct current (DC) or by electrical impedance spectrometry (EIS) using alternating current (AC) while the membrane is immersed in a NaCl or KCl solution [10–18]. Because concentration polarization occurs due to ionic current flow,

diffusion boundary layers (DBLs) evolve on both sides of the membrane and are characterized by a change in the electrolyte concentration near the solution-membrane interface. As a result, the measured membrane resistance varies significantly when the measurement is taken under different operating conditions (i.e., different external solution concentrations or applied current densities) [12,19,20]. Previous studies treated this complexity as the overpotential and modeled using EIS, while the overall system resistance was estimated using experimental values [6,12,19,21]. The boundary layer effects near the solution-membrane interface have also been investigated in several reported studies [17,22–25].

However, reliable information on the concentration-dependency of membrane resistance is lacking, and the effect of electrical current density has not been explored in detail [22,26]. For applications such as RED and electrodialysis, each membrane is not in contact with electrolyte solution of same concentration on both sides and the electrical current in the system may vary. Consequently, the commonly used value of membrane resistance measured under these conditions does not represent the apparent resistance of a membrane in these systems. An RED system model using this approach is not fully applicable if the internal resistance is determined on the basis of the

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summation of the separately measured resistances of the membrane and other components [12,17,27–30].

Furthermore, the electrochemical properties of membrane material and its relationship to resistance is important to the synthesis of the membrane. The extent of improvement attainable through optimization of membrane properties can be limited by the environment of membrane application. The results of this limitation have led to a need for further research on how the membrane properties can be better managed so as to benefit from the environment. Therefore, this article aims to develop a novel membrane resistance model that provides a comprehensive description of the apparent resistance of cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs). The model is derived directly from the membrane's electrochemical properties under different operating conditions.

2. Model development

According to the classical electrochemical analysis of a solution with diffusion limiting transport, the solution-membrane interface concentration of salt varies with the density of the electrical current flowing through the solution [25,30]. In a sodium chloride solution, Na^+ and Cl^- ions carry the electrical current fairly equally. However, in the membrane phase, only counter-ions are the major carriers of current. The difference in the counter-ion transport numbers in the solution and in the membrane phase causes a gradient of concentration perpendicular to the membrane plane that is usually called "concentration polarization" [3]. As a result, on one side of the membrane, the counter-ion (ions having opposite charge compared to membrane bulk material) is approaching the membrane-solution interface. Because of a faster transport of counter-ion across the membrane and the migration of co-ion (ions with the same charge as membrane bulk material), electroneutrality is maintained and generates a depletion of salt concentration. On the other side accumulation of counter-ion due to a sudden decrease of transport accompanied with migration of co-ion maintains the electroneutrality and generates an accumulation of salt concentration. The concentration obeys a linear decrease while approaching the membrane surface at a steady state when transport is stabilized.

2.1. Non-ohmic resistance in DBLs

As shown in Fig. 1, the salt concentration at the solution-membrane interface is a function of the applied current density (i) and limiting current density (i_{lim}). Eq. (1a) describes the concentration variation on the depleting side of DBL and Eq. (1b) on the accumulating side [25,31].

$$C_1^b(i) = C_0 \left(1 - \frac{i}{i_{lim}} \right)$$
(1a)

$$C_2^b(i) = C_0 \left(1 + \frac{i}{i_{lim}} \right)$$
(1b)

where C is the concentration of salt (mol/L), the subscripts 1 and 2 indicate the depleting and accumulating sides, respectively, and C_0 is the concentration of the bulk solution. The superscript b indicates that the concentrations concerned at the solution-membrane interface.

At steady state, the concentration gradient in the DBL is assumed to be constant [31,32]. From Fig. 1, the concentration in the DBL as a function of distance (x) to the interface can be expressed as:

$$C_1(x) = C_1^b + \frac{C_1^b - C_0}{\delta} x$$
(2a)

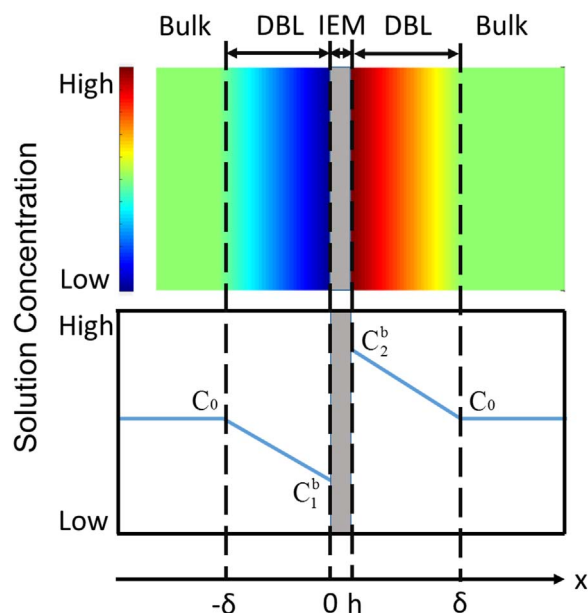$$C_2(x) = C_2^b - \frac{C_2^b - C_0}{\delta}(x - h)$$
(2b)

Fig. 1. Diffusion boundary layer (DBL) near the surface of a cation-exchange membrane and the salt concentration distribution in different layers at steady state. Current direction is to the right. This illustrates the common situation in which the membrane resistance is measured with the same bulk solution concentration on both sides of the membrane using direct current. The left side shows a depleting side of DBL and the right side shows an accumulating side of DBL. (The schematic is not drawn to scale.).

where h is the thickness (m) of the membrane and δ is the thickness (m) of the DBLs as shown in Fig. 1. Because the flow rate and dimension of equipment are kept the same for different situations studied in this work, the thickness of DBLs on both sides are assumed to be the same as determined by flow rate [33–35]. Then, the resistances of the electrolyte (R_{L1} and R_{L2} in $\Omega\,m^2$) from the DBLs on each side of the membrane are given by the integral over the thickness of each DBL [25]:

$$R_{L1} = \int_{-\delta}^{0} \frac{1}{\kappa_1} dx = \int_{-\delta}^{0} \frac{1}{\Lambda \cdot C_1(x)} dx = \frac{\delta}{\Lambda \cdot (C_0 - C_1^b)} \ln \frac{C_0}{C_1^b}$$
(3a)

$$R_{L2} = \int_{h}^{h+\delta} \frac{1}{\kappa_2} dx = \int_{h}^{h+\delta} \frac{1}{\Lambda \cdot C_2(x)} dx = \frac{\delta}{\Lambda \cdot (C_0 - C_2^b)} \ln \frac{C_0}{C_2^b}$$
(3b)

where κ_1 and κ_2 are the conductivities (S/m) of the DBLs, and Λ is the molar conductivity of the salt solution (S m^3/mol). The x-axis is the direction perpendicular to the membrane surface. Combining Eqs. (3a) and (3b), and substituting Eqs. (1a) and (1b) into Eqs. (3a) and (3b), we obtain

$$R_L = \left(\frac{\delta}{r \cdot \Lambda} \ln \frac{1 + r}{1 - r} \right) \cdot \frac{1}{C_0}$$
(4)

$$r = \frac{i}{i_{lim}}$$
(5)

The above equation represents a change in the electrolyte conductivity as a result of concentration polarization. If the transport numbers of cations and anions are different in the solution phase (e.g., NaCl solution), a diffusion potential exists, and are denoted as E_{d1} and E_{d2} indicating depleting and accumulating sides, respectively. The resultant resistances can be expressed as:

$$R_{d1} = \frac{E_{d1}}{i} = -\frac{RT}{iF} \Delta t \ln \frac{a_0}{a_1^b}$$
(6a)

$$R_{d2} = \frac{E_{d2}}{i} = -\frac{RT}{iF} \Delta t \ln \frac{a_2^b}{a_0}$$
(6b)

Here, Δt is the difference of ion transport numbers in the solution