An Integrative Modeling and Experimental Study on the Ionic Resistance of Ion-Exchange Membranes

Bopeng Zhang^a, Jin Gi Hong^b, Shihua Xie^a, Shuman Xia^c, Yongsheng Chen^{a}*

^a School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

^b Department of Civil Engineering and Construction Engineering Management, California State University, Long Beach, CA, 90840, United States

^c The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

* Corresponding author.

E-mail: yongsheng.chen@ce.gatech.edu; Phone: (+1) 404-894-3089

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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 to 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.

Keywords: Ionic resistance; ion-exchange membranes; diffusion boundary layer; reverse electrodialysis.

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]. In this application, 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

45 effects near the solution-membrane interface have also been investigated in several
46 reported studies [17, 22-25].

47 However, reliable information on the concentration-dependency of membrane resistance
48 is lacking, and the effect of electrical current density has not been explored in detail [22,
49 26]. For applications such as RED and electrodialysis, each membrane is not in contact
50 with electrolyte solution of same concentration on both sides and the electrical current in
51 the system may vary. Consequently, the commonly used value of membrane resistance
52 measured under these conditions does not represent the apparent resistance of a
53 membrane in these systems. An RED system model using this approach is not fully
54 applicable if the internal resistance is determined on the basis of the summation of the
55 separately measured resistances of the membrane and other components [12, 17, 27-30].

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

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

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

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.

Figure 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.)

102 At steady state, the concentration gradient in the DBL is assumed to be constant [31, 32].

103 From Figure 1, the concentration in the DBL as a function of distance (x) to the interface

104 can be expressed as:

$$105 \quad C_1(x) = C_1^b + \frac{C_1^b - C_0}{\delta} x \quad (2a)$$

$$106 \quad C_2(x) = C_2^b - \frac{C_2^b - C_0}{\delta} (x - h) \quad (2b)$$

107 where h is the thickness (m) of the membrane and δ is the thickness (m) of the DBLs as

108 shown in Figure 1. **Because the flow rate and dimension of equipment are kept the same**

109 **for different situations studied in this work, the thickness of DBLs on both sides are**

110 **assumed to be the same as determined by flow rate** [33-35]. Then, the resistances of the

111 electrolyte (R_{L1} and R_{L2} in $\Omega \cdot m^2$) from the DBLs on each side of the membrane are given

112 by the integral over the thickness of each DBL [25]:

$$113 \quad R_{L1} = \int_{-\delta}^0 \frac{1}{\kappa_1} dx = \int_{-\delta}^0 \frac{1}{\Lambda \cdot C_1(x)} dx = \frac{\delta}{\Lambda \cdot (C_0 - C_1^b)} \ln \frac{C_0}{C_1^b} \quad (3a)$$

$$114 \quad R_{L2} = \int_h^{h+\delta} \frac{1}{\kappa_2} dx = \int_h^{h+\delta} \frac{1}{\Lambda \cdot C_2(x)} dx = \frac{\delta}{\Lambda \cdot (C_0 - C_2^b)} \ln \frac{C_0}{C_2^b} \quad (3b)$$

115 where κ_1 and κ_2 are the conductivities (S/m) of the DBLs, and Λ is the molar conductivity

116 of the salt solution ($S \cdot m^3/mol$). The x -axis is the direction perpendicular to the membrane

117 surface. Combining Eqs. 3a and 3b, and substituting Eqs. 1a and 1b into Eq. 3, we obtain

$$118 \quad R_L = \left(\frac{\delta}{r \cdot \Lambda} \ln \frac{1+r}{1-r} \right) \cdot \frac{1}{C_0} \quad (4)$$

$$119 \quad r = \frac{i}{i_{lim}} \quad (5)$$

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:

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

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

Here, Δt is the difference of ion transport numbers in the solution phase. Adding Eqs. 6a and 6b together and substituting Eqs. 1a and 1b to replace the concentration term, we can obtain Eq. 7.

$$R_d = \frac{RT}{iF} \Delta t \cdot \ln \frac{a_2^b}{a_1^b} = \frac{RT}{iF} \Delta t \cdot \ln \frac{\gamma_2 C_2^b}{\gamma_1 C_1^b} = \frac{RT}{iF} \Delta t \left(\ln \frac{1+r}{1-r} + \ln \frac{\gamma_2}{\gamma_1} \right) \quad (7)$$

Here, γ indicates the activity coefficient. The minus sign, which indicates that the direction of the potential is opposite to that of the direct of current, is dropped for resistance calculation. While the concentration on both sides are not the same, as in the case of concentration polarization, a membrane potential E_m^{DBL} is generated. The potential is reflected as a resistance that can be expressed in Eq. 8 [36]. The minus sign is dropped here as well as in resistance calculation.

$$R_m^{DBL} = \frac{E_m^{DBL}}{i} = \frac{RT}{iF} \Delta \bar{t} \cdot \ln \frac{a_2^b}{a_1^b} = \frac{RT}{iF} \Delta \bar{t} \cdot \ln \frac{\gamma_2 C_2^b}{\gamma_1 C_1^b} = \frac{RT}{iF} \Delta \bar{t} \left(\ln \frac{1+r}{1-r} + \ln \frac{\gamma_2}{\gamma_1} \right) \quad (8)$$

where $\Delta \bar{t}$ represents the difference of transport numbers of counter-ions and co-ions in the membrane phase.

140

141 2.2 Resistance of Membrane Bulk Material

142 Because only the solution phase in the membrane structure is conductive, the transport
 143 properties considered here concern only the membrane-phase solution and salt ions inside
 144 the solution. Also, the electrochemical properties of the membrane are treated as being
 145 homogeneous.

146 Using the 1-D Nernst-Planck equation, we only deal with the case where the valence of
 147 the ions is unity (because sodium chloride is the only salt used here). Also, we assume a
 148 steady-state convection; thus, the DBL is stable near the membrane solution interface.
 149 Finally, the diffusion and migration can be described using the Nernst-Einstein equation
 150 (Eq. 9), for a species k :

$$151 \quad u_k = \frac{D_k F}{RT} \quad (9)$$

$$152 \quad J_k = -D_k \frac{dC_k}{dx} - u_k C_k \frac{d\varphi}{dx} = -D_k \frac{dC_k}{dx} - D_k \frac{C_k F}{RT} \frac{d\varphi}{dx} \quad (10)$$

153 where J_k is the flux of ions (mol/(m²·s)) in the solution, D_k is the diffusivity of an ion
 154 species (m²/s), φ is the external electrical potential applied to the system (V), u_k is the
 155 mobility of ions (m²/(V·s)), R is the gas constant, F is the Faraday constant, and T is the
 156 temperature (K). Moreover, the diffusion term can be further defined such that the current
 157 density is [30]:

$$158 \quad i = F \sum_k J_k = -F^2 \sum_k \frac{C_k D_k}{RT} \left(\frac{RT}{C_k F} \frac{dC_k}{dx} + \frac{d\varphi}{dx} \right) = -F^2 \sum_k \frac{C_k D_k}{RT} \left[\frac{d}{dx} \left(\frac{RT}{F} \ln C_k \right) + \frac{d\varphi}{dx} \right] \quad (11)$$

Both terms in the bracket have the dimension of potential gradient and thus can further be expressed in a combined form (the electrochemical potential gradient if the pressure components are neglected). Let the combined potential be Φ (V), then,

$$i = -F^2 \sum_k \frac{C_k D_k}{RT} \frac{d\Phi}{dx} \quad (12)$$

However, Ohm's law states that the conductivity κ (S/m) is:

$$i = \kappa \frac{d\Phi}{dx} \quad (13)$$

Thus, by substituting Eq. 12 into Eq. 13, the conductivity of the membrane phase solution is:

$$\kappa = F^2 \sum_k \frac{C_k^m D_k^m}{RT} \quad (14)$$

The superscript m indicates that the value is for the membrane phase. Note that the minus sign only indicates the direction of the current in Eq. 12 and is neglected in Eq. 13. Finally, if we assume the concentration is **uniform** within the membrane phase for both counter- and co-ions, we can conclude that the ionic resistance of the solution in the membrane phase (R_m) is:

$$R_m = \int_0^h \frac{dx}{\kappa^m} = \int_0^h \frac{RT}{F^2 \cdot (D_{ct}^m C_{ct}^m + D_{co}^m C_{co}^m)} dx = \frac{hRT}{F^2 \cdot (D_{ct}^m C_{ct}^m + D_{co}^m C_{co}^m)} \quad (15)$$

The subscripts ct and co indicate counter-ion and co-ion, respectively. The counter- and co-ion concentrations in the membrane phase can be derived from the Donnan equilibrium [37]:

$$C_{ct}^m = \frac{C_{fix}}{2} + \sqrt{\left(\frac{C_{fix}}{2}\right)^2 + (C_i^\delta)^2} \quad (16a)$$

$$C_{co}^m = -\frac{C_{fix}}{2} + \sqrt{\left(\frac{C_{fix}}{2}\right)^2 + (C_i^\delta)^2} \quad (16b)$$

where C_{fix} is the fixed charge density (FCD) (eq./L) in the ion-exchange membrane. It is calculated as the ratio of ion exchange capacity (IEC) to swelling degree (SD):

$$C_{fix} = \frac{IEC}{SD} \quad (17)$$

The co-ion concentration can be assumed to be negligible in the membrane due to Donnan exclusion. In the concentration range concerned in this study, co-ion concentration is two orders of magnitude lower than counter-ion concentration in the membrane [36]. Furthermore, from Eq. 10a, if the concentration at the solution-membrane interface C^b is relatively small compared to C_{fix} , the counter-ion concentration is very close to C_{fix} . Then Eq. 9 becomes:

$$R_m = \frac{hRT}{F^2 \cdot (D_{ct}^m C_{ct}^m + D_{co}^m C_{co}^m)} \cong \frac{hRT}{F^2 D_{ct}^m C_{fix}} \quad (18)$$

The assumption here is well justified with a typical membrane used in this study. For example, the sPPO membrane has a fixed charge density of 5.15 mol/L using Eq. 17, which results in a counter-ion concentration of 5.20 mol/L in the NaCl solution of 0.5 mol/L as indicated in Eq. 16a. This result is in agreement with the model used in the electrodialysis field [18, 23]. Furthermore, because the counter-ion considered can be different in CEMs and AEMs, the derivation is valid to either type of IEM. For simplicity, the membrane-property-related parameters D_{ct}^m and C_{fix} are denoted as a single parameter M .

2.3 The Measurement of Resistance Under DC Conditions

199 The common measurement of membrane resistance using the DC method is severely
 200 affected by the DBL; in fact, the resulting resistance is partly caused by the DBL even
 201 under vigorous stirring [19]. If the resistance is measured with the same concentration of
 202 solution on both sides of the membrane, the reported result (R_0) is the difference between
 203 the experimental (R_E) and blank (R_{BL}) resistances compensated by the solution resistance
 204 that has the same resistance of solution with thickness h [38]:

$$205 \quad R_0 = R_E - R_{BL} + \frac{h}{\Lambda \cdot C_0} \quad (19)$$

206 We neglect all resistances other than the resistance raised due to the formation of DBL
 207 because subtraction of the blank removes such resistances from the final result. During
 208 DC measurement of membrane resistance with the same bulk solution concentration on
 209 both sides of the membrane, the combination of the four resistances from Eqs. 4, 7, 8 and
 210 18 gives the total resistance of the membrane as it adds up the change of resistance in
 211 DBL, the diffusion generated resistance, and the membrane-potential-related resistance:

$$212 \quad R_E = R_L + R_d + R_m^{DBL} + R_m \quad (20)$$

213 The blank resistance to be subtracted is calculated as the resistance of the solution that
 214 replaces the two DBLs and the membrane bulk in thickness:

$$215 \quad R_{BL} = \frac{2\delta + h}{\Lambda \cdot C_0} \quad (21)$$

216 Thus, Eq. 19 becomes:

$$217 \quad R_0 = a \cdot \frac{1}{C_0} + b \quad (22a)$$

$$218 \quad a = \frac{\delta}{r \cdot \Lambda} \ln \frac{1+r}{1-r} - \frac{2\delta}{\Lambda} \quad (22b)$$

$$b = \frac{hRT}{F^2 M} + \frac{RT(\Delta t + \Delta \bar{t})}{ri_{\text{lim}} F} \cdot \left(\ln \frac{1+r}{1-r} + \ln \frac{\gamma_2}{\gamma_1} \right) \quad (22c)$$

As a result, the resistance measured by the DC method is dependent on the external solution concentration C_0 . The linear relationship between the measured resistances and the reciprocal of the bulk solution concentration is expected. Furthermore, it can be proved using L'Hôpital's rule that the “ a ” term in front of the reciprocal of concentration approaches to two when r approaches zero (i.e., no electrical current flow).

3. Materials and Methods

3.1 Synthesis of sPPO membrane

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO), analytical standard grade, was purchased from Sigma Aldrich. The PPO sulfonation was carried out according to the procedure described in the literature [8, 39]. Chloroform (Sigma Aldrich, anhydrous, 99 %) and methanol (Sigma Aldrich, anhydrous, 99.8 %) were used as solvents, and chlorosulfonic acid (VWR, 99%) was used as the sulfonating agent.

3.2 Membrane resistance measurement using DC

Membrane samples were placed between two PMMA (poly(methyl 2-methylpropenoate)) cells each with a volume of 460 ml (7.6 cm × 7.6 cm × 8 cm) (Figure 2). Sodium chloride solution was supplied at a flow rate of 60 ml/min by a Masterflex[®] peristaltic pump (Cole-Parmer, USA). The membrane had an effective area of 7.9 cm². Before the measurement, membranes were equilibrated with the corresponding solution (0.01 mol/L–0.5 mol/L NaCl) for at least 24 h. On each end of the cell, two titanium mesh electrodes coated with iridium were used as working and counter electrodes; two silver/silver chloride electrodes were used as reference electrode and placed in Luggin capillaries at fixed positions with a tip-to-tip distance of 3 mm on two sides of the membrane. Direct electrical current was applied to the system in a galvanostatic mode with six current steps using an Ivium potentiostat (Vortex[®], Ivium Technologies, the Netherlands). Each step was maintained for at least 30 seconds to reach a stable reading. The measured current-voltage curve was used to obtain membrane resistance based on the slope of the curve [13]. Because the limiting current density is a function of solution

concentration, we used different current steps for different solution concentrations. For 0.01 mol/L solution, the maximum current density of 3.79 A/m^2 was achieved after six equal steps; for 0.017 mol/L solution, the maximum current density was 7.59 A/m^2 in six steps; for 0.05 mol/L and 0.1 mol/L solutions, the maximum current density was 26.5 A/m^2 in six steps; and for 0.5 mol/L solution, the maximum current density was 75.8 A/m^2 in six steps. The current density used was kept far below the limiting current density so that the current density effect was not obvious during the measurement except for the cases of 0.01 mol/L and 0.017 mol/L solutions. In these two situations, the current density ratio r reached 0.55. Three membranes of the same kind were measured as replicates in all of the following measurements.

Figure 2. Experimental setup for DC and AC measurements. Titanium electrodes coated with Iridium are pointed as ‘Electrode’; Ag/AgCl electrodes are placed in the ‘Luggin capillary’.

262

263 3.3 Membrane resistance measured by varying current density using DC

264 To study the effect of applied current density on the resistance measurement, a method
265 has been developed to measure the resistance at a certain applied current density instead
266 of using the slope of I-V curve at different current densities. A similar method has been
267 reported in the literature [40]. The resistance is derived from the potential drop after a
268 single current jump. Sufficient time was allowed to reach a steady voltage state to reach
269 the steady-state (Figure 3). Multiple steps were applied to obtain resistance under
270 different current density ratios. In this approach, the resistance at a constant current
271 density ratio can be obtained.

272

273

274 **Figure 3.** Schematic representation of method used to study the effect of current density.
275 Potentiostat controls the time and height of each current density step, and the total

potential drop is measured until the steady state is reached. Used current density values depend on the limiting current density of each membrane to obtain different current density ratios r .

3.4 Membrane resistance measurement using AC

With the same setup, alternating current (AC) was applied to the system. Electrical impedance spectroscopy was used to analyze results based on the model. Applied frequency was set to 1000 Hz with five different current amplitudes from 1.8 A/m² to 35.5 A/m² with a step of 7 A/m². When the AC frequency was in this range, the membrane bulk resistance along with solution resistance was measured [12, 15, 21]. A following experiment without membrane was performed as a blank run. The pure membrane resistance was calculated as the difference between the impedances obtained in these two experiments.

3.5 Modeling methodology

The constants used in the model are listed in Table 1. The molar conductivity of NaCl is assumed to be constant in the concentration range discussed in this paper. The activity coefficients were calculated based on the Debye–Hückel equation and the Davies equation within their ranges of applicability, respectively. Simulation and graph generation were conducted using MATLAB® R2013a (MathWorks, Natick, MA, USA) and Microsoft Excel®. The area resistance is calculated based on Eq. 19. The NaCl concentration range is between 0.010 mol/L and 0.500 mol/L to fall within the conditions practically encountered during RED power generation. The temperature used in the calculation is assumed to be 298±1 K (25±1 °C). Membrane properties (except resistance) were taken as reported for frequently used IEMs in RED studies: CMX and

300 AMX membranes were reported in the study by Dlugolecki et al. (2010) [14], and FKS
301 cation and FAS anion (FuMA-Tech, Bietigheim-Bissingen, Germany) membrane
302 properties along with SELEMIONTM (AGC Engineering, Japan) according to
303 manufacturer's specifications [41]. These properties are listed in Table 2.

304 **Table 1.** Nomenclature in the model simulation

Parameter	Description	Value/Notes
F	Faraday constant (s·A/mol)	96485
R	Gas constant (J·mol/K)	8.314
T	Temperature (K)	298
Λ	Molar Conductivity of NaCl Solution (298 K) (S·m ² /mol)	0.01265 *
Δt	Difference of transport numbers of sodium ion and chloride ion in water solution	-0.22 for CEM and 0.22 for AEM
$\Delta \bar{t}$	Difference of transport numbers of sodium ion and chloride ion in membrane phase	Estimated from permselectivity [35, 36]**
δ	Thickness of DBL (m)	1.0E-3 (fit value from FKS membrane, used for other membranes)
h	Thickness of membrane (m)	-
D_{ct}^m	Diffusivity of counter ion in membrane phase (m ² /s)	-
C_{fix}	Fixed charge density of membrane (eq./L)	-
a_1^b, a_2^b, a_0	Activities of sodium chloride on both sides of membrane and bulk solution	Debye–Hückel model or Davies model within their ranges of applicability
M	Membrane property parameter (m ² ·eq./(L·s))	The product of D_{ct}^m and C_{fix}
i	Applied current density (A/m ²)	-
i_{lim}	Limiting current density (A/m ²)	Measured at 70.57 (FKS), 102.9 (FAS), and 68.5 (sPPO) in 0.1 mol/L NaCl solution; assuming changing linearly with respect to solution concentration [36].
r	Ratio of applied current density to limiting current density	Within the range of 0 to 1
C_o	Bulk solution concentration (mol/L)	-
γ	Activity coefficient	-
R_L	Resistance due to the change of electrolyte concentration in diffusion boundary layer (Ω·m ²)	-
R_d	Resistance due to diffusion potential formed in diffusion boundary layer (Ω·m ²)	-
R_m^{DBL}	Resistance due to membrane potential formed across membrane (Ω·m ²)	-
R_0	Measure membrane resistance (Ω·m ²)	-
R_m	Membrane bulk resistance; assumed to be the AC measurement result (Ω·m ²)	-
R_E	Experimental resistance result (before subtracting control run) (Ω·m ²)	-
R_{BL}	Control run of resistance measurement (Ω·m ²)	-

305 * Source: Barragan and Bauza [42]

306 ** An approximate relationship has been used here $P \approx \frac{\bar{t} - t}{1 - t}$, where, P is the
 307 permselectivity of membrane, t is the transport number of counter-ion in water phase and
 308 $\bar{t}$ is the transport number of counter-ion in membrane phase [35, 36].

309 **Table 2.** Properties of Related Ion Exchange Membranes

	IEC (meq/g dry membrane)	Permselectivity (%)	SD (%)	Thickness (μm)	References
FKS	1.47	98.3	33-41	20 - 63	
FAS	> 1	94.6	22-25	20 - 54	
CMX	1.64	92.5	21.5	181	[14]
AMX	1.30	91.0	16.4	138	[14]
sPPO	1.90	89.9	36.9	16 - 94	

310

4. Results and Discussion

4.1 Membrane resistance measured using AC

FKS, FAS, and sPPO membranes of different thicknesses were measured using the AC method. A linear relationship of area resistance to thickness is clearly illustrated in Figure 4. From Eq. 22, only the bulk resistance (term in value b) dominates when an alternating electrical field with high frequency (1000 Hz in this case) exists, because the polarization effect is not evident when there is no net migration of ions in any direction. Therefore, the membrane property parameter M (combined indicator of fixed charge density and interaction of counter-ions with membrane bulk material) is the only property that affects the membrane resistance. For a certain type of membranes (e.g., sPPO membrane made from the same batch of source material), M remains constant regardless of the thickness of the membrane. Consequently, the membrane resistance measured using the AC method should exhibit a linear relationship against the thickness of the membrane. The same assumption can be applied to commercial FKS and FAS membranes to evidence the observed phenomena. In Figure 4, the interceptions on the y axis are all relatively small (i.e., 0.09 for FKS, 0.07 for FAS, and 0.04 for sPPO). When the thickness of the membrane approaches zero, the bulk resistance is also approaching zero (Eq. 18). The slopes of these lines are different, indicating different membrane property parameters M .

Figure 4. Membrane resistance measured using AC against membrane thickness. For each kind of membrane, four different thicknesses were tested. Error bars show the 95% confidence interval of replicates during resistance and thickness measurements.

This linear relationship has been implied in the literature, but not specifically proved because different membrane properties were compared [2]. Assuming that the membrane property parameter (M) is constant with a given membrane material, thinner membranes should be advantageous as long as mechanical strength permits. However, as will be discussed later, resistance measured using AC without significant boundary layer effect presents the membrane bulk resistance and is, therefore, not a proper indicator of membrane resistance in a system with DC current flow. By using this AC resistance to represent membrane bulk resistance, term b in Eqs. 22 can be further evaluated in DC studies.

4.2 External concentration effect

Membrane resistance was measured when the membrane was in contact with NaCl solution of different concentrations. The resistance obtained from AC studies was used as bulk resistance $\frac{hRT}{F^2M}$ (as in term b of Eq. 22) for each membrane. An optimized hydrodynamic parameter (DBL thickness δ) and current density ratio r were obtained from fitting FKS membrane measurement results as 1.0 mm and 0.54, respectively. Results were not significantly different if FAS or sPPO data was used as the fitting data (Supporting Information). The current density ratio is relative to the limiting current density of FKS here. The current density ratio for different membrane varied with respect to different limiting current densities (Table 1). Therefore, even the current applied during the measurement was kept the same for different membrane, the resulting r values were different for different membranes. The same δ was used in all cases. As shown in Figure 5, simulation results using the model correlate well with experimental data for the FKS membrane, and the prediction matches well for FAS and sPPO data. The coefficients of variance (R^2) are 0.951, 0.938, and 0.998 for FKS, FAS, and sPPO membranes, respectively.

The assumption of the same DBL thickness for different membranes is appropriate because both the solution flow rate and the distance between the two Luggin capillaries were fixed in this study. Therefore, only the local flow pattern near the membrane surface would affect the hydrodynamic environment [34, 43]. Since the same testing cell was used in all experiments (Figure 2), local variations should not be a significant concern. The current density ratio r used in the simulation and prediction was well justified for low concentration situations (0.01 mol/L and 0.017 mol/L) as the current density used

during the measurement could reach over half of the limiting current density. According to Eq. 22, when the bulk solution concentration (C_0) increases, the effect of current density diminishes rapidly. In fact, the current density ratio r varying under 0.55 did not result in a significant difference of predicted resistance.

Figure 5. Concentration dependency of the membrane resistance is measured using DC on FKS, FAS, and sPPO membranes. Simulation curve and experimental data are compared and residues are presented.

To further validate the model, the simulation of resistances was fit to data reported in Dlugolecki et al. (2010) for the commercially available CMX and AMX equilibrated in different concentrations of NaCl solution [14]. The simulation curves matched well with the measured resistances at various NaCl concentrations as seen in Figure 6. Note, however, that a different value of $r = 0.36 (i/i_{lim})$ (Eq. 19) was used for best fit. The difference in applied current density (i) is reasonable since the measuring current density does not exceed the limiting current density ($r < 1$) [14, 19]. The coefficients of variance (R^2) are 0.993 and 0.985 for CMX and AMX membrane fittings, respectively.

The increase of measured resistance along with the decrease of external solution concentration has also been shown in other studies. For example, in the model developed by Kim et al., (2013) [44], the membrane resistance has a linear relationship with the reciprocal of external solution concentration. Their model was not able to explain the situation when the membrane resistance plateaus at a certain level under sufficiently high salt concentration instead of approaching zero. On the other hand, the model presented in this work treats the term a in Eq. 22 containing $1/C_0$ as the term affected by external concentration, which decreases rapidly as the bulk concentration increases. However, the last term in Eq. 22, $\frac{hRT}{F^2M}$ (membrane bulk resistance) stays almost the same, which explains the plateaus. Galama et al. (2014) also fit the resistance trend using a similar form as seen in Eq. 22, but no physical meanings associated with the fitting parameters were proved [21].

The strength of the presented model lies on the prediction of apparent resistance of membrane when the current density varies. Obviously, the DBL thickness as an indicator of hydrodynamic environment and membrane property M and limiting current density in a given concentration have to be given as inputs. Generally, M may change according to external concentration. However, because of the Donnan equilibrium, the assumption that the counter-ion concentration in the membrane phase is relatively stable over a wide concentration range is valid, especially when the concentration concerned is significantly lower than the fixed charge density as shown in Eq. 16a [37].

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410

411 **Figure 6.** Simulation of the concentration dependency of CMX and AMX membrane
 412 resistance compared to the data reported in Dlugolecki et al. (2008). Residues of the data
 413 to the model simulation values are also presented.

414

415 **4.3 Current density and its effect on DC measurement**

Membrane resistance measured using different current densities in 0.1 mol/L NaCl solution are compared with the model prediction of resistance at different current densities in Figure 7. Using the same δ , the current density ratio r was calculated based on different limiting current densities for FKS and FAS membranes as measured in this study (Table 1). The model shows a relatively good prediction at r values studied with R^2 of 0.930 for FKS and 0.844 for FAS. Variation of resistance with respect to the r value showed an apparent increasing trend when higher r values were applied. As depicted in Eq. 22, current density applied to the system directly affects the concentration distribution within the DBL which alters the resistance of the DBL and results in a non-ohmic resistance.

Concentration polarization has been well studied, but the effect of applied current density on the membrane resistance measurement is rarely researched in literature [11, 14, 19, 22]. A common practice of resistance measurement applies DC at different current densities to a membrane equilibrated in a solution of certain concentrations [12, 14, 25]. Under this condition, even though the DBL thickness can be controlled hydrodynamically, the resistance resulting from the DBL would vary because different current densities are applied. The extent of concentration polarization under various current densities causes inaccuracies in the results in applications of electrodialysis and RED. Barragan and Ruiz-Bauza (1998) reported a model simulating the change in resistance due to the concentration polarization near the solution-membrane interface for electrodialysis application. However, not all non-ohmic resistance was considered in their model, and the membrane bulk resistance was not associated with membrane properties. In an electrodialysis system, high current ratio situations are common. As indicated in

439 this study, membrane resistance behavior is considerably different from measurements
440 [3].

Figure 7. The effect of applied current density on the measured membrane resistance. Predictive curve and experimental data are compared and residues are presented.

4.4 Implication to Membrane Synthesis and IEM Applications

Because of the dependency of resistance to membrane thickness, a high performance ion-exchange membrane should have the least thickness possible in a specific application, as

long as the mechanical strength permits. Given a fixed membrane thickness, electrochemical properties characterized by M determines the resistance. However, as simulated in **Figure 8**, improvement of membrane properties can be easily diminished when the system is applied under low electrolyte concentration or at high current density ratio. The resistance from the DBLs, as a combination of resistance due to change of electrolyte concentration and resistance generated from diffusion potential and membrane potential, is more pronounced when the external solution concentration is lower, whereas the resistance of the membrane bulk stays the same over the full concentration range examined. Similarly, experimental data from RED stack design studies indicate that the diluted solution compartment contributes the most to the internal resistance [19, 45]. Therefore, improvement of performance for a system such as RED (usually concentration level of fresh water encountered) requires not only superb membrane properties, but also practical approaches to decreasing concentration polarization. In an electrodialysis system for desalination, the situation is even worse because the applied current density could easily be close to the limiting current density.

Figure 8. Simulation of contributions to the apparent resistance of a FKS membrane. DBL thickness is set to 1.0 mm. “Bulk” denotes the resistance from membrane material (first term in Eq. 22c); “Concentration change oriented” denotes the resistance calculated from Eq. 22b; and “Potential oriented” denotes the resistance calculated from the second

470 term in Eq. 22c. (a) With the same $r = 0.5$, the simulated membrane resistance in NaCl
471 solution of a concentration varies from 0.01 mol/L to 0.21 mol/L. (b) With the same NaCl
472 solution concentration of 0.1 mol/L, the simulated membrane resistance when applied has
473 a current density ratio that can vary from 0.17 to 0.97.

5. Conclusions

A model of internal ionic resistance in a RED system has been developed by considering the DBL and IEM bulk properties. The model explains the widely reported phenomena theoretically and verifies them with experimental and reported data. Prediction of membrane resistance matched well with experimental data on commercial FKS and FAS membranes, as well as in-house fabricated sPPO membranes.

The increase in membrane resistance in a solution with decreased concentration is well explained by the contribution of the DBL to the overall membrane resistance. The model also reveals a linear relationship between the measured membrane resistance and the reciprocal of the external solution concentration when using the DC method. Moreover, the model considers the influence of applied current density, which may affect the resistance of an IEM, especially when the salt concentration is relatively low (<0.1 mol/L) and the applied current density is higher than 90% of the limiting current density ($r > 0.9$).

To the best of our knowledge, few studies have focused on quantifying the contributions of the DBL and membranes in terms of their ionic resistance with respect to the current density. Using the model presented here, a practical estimation of the resistance of systems such as electrodialysis and RED would be more accurate.

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