Salt Concentration Differences Alter Membrane Resistance in Reverse Electrodialysis Stacks

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S Supporting Information

ABSTRACT: Membrane ionic resistance is usually measured by immersing the membrane in a salt solution at a single, fixed concentration. While salt concentration is known to affect membrane resistance when the same concentration is used on both sides of the membrane, little is known about membrane resistance when the membrane is placed between solutions of different concentrations, such as in a reverse electrodialysis (RED) stack. Ionic resistance measurements obtained using Selemion CMV and AMV that separated sodium chloride and ammonium bicarbonate solutions of different concentrations were greater than those measured using only the high-concentration solution. Measured RED stack resistances showed good agreement with resistances calculated using an equivalent series resistance model, where the membranes accounted for 46% of the total stack resistance. The high area resistance of the membranes separating different salt concentration solutions has implications for modeling and optimizing membranes used in RED systems.
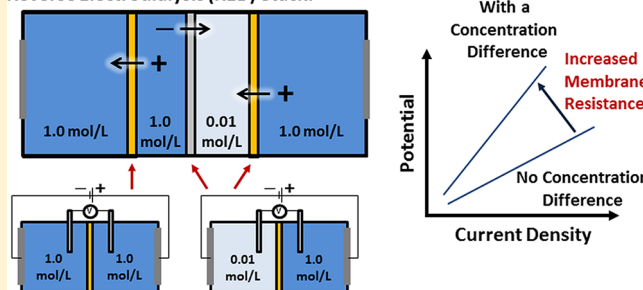
INTRODUCTION

Reverse electrodialysis (RED) is a promising technology for converting salinity gradient energy into electricity.[1−6] RED stacks contain alternating anion and cation exchange membranes (AEMs and CEMs) that separate salt solutions of different concentrations.[1,3,4] Selective transport of ions through the membranes creates an electric potential across pairs of AEMs and CEMs, and large numbers of cell pairs are used in a stack to increase the total potential and drive electric current through an external circuit.[3,4] Many studies have focused on improving performance by optimizing the hydrodynamics of flow between the membranes,[1,7] but performance and efficiency of a RED stack also depend on the ionic resistance of the membranes.[8] Membrane ionic resistance can be tuned by changing the membrane polymer chemistry and/or membrane form factor.[9−13] The ion transport properties of a given membrane, however, are also sensitive to the concentration of salt surrounding the polymer (i.e., the feed solutions in a RED process).[14,15] Therefore, the influence of different salt concentrations on either side of the membrane on ion transport properties must be studied to improve our understanding of the role of membranes in RED.

The ionic resistance of ion exchange membranes, such as those for RED, is usually measured with the membrane immersed in an electrolyte solution at a single fixed concentration.[2,16] The electrolyte concentration is chosen to make it much more conductive than the membrane, so that the difference between the Ohmic resistances of the solution and the membrane is large. Salt solutions at concentrations of ≥0.5 mol/L are typically used to characterize the ionic resistance of membranes.[2,16] However, membrane resistance substantially increases when using solutions that have lower salt concentrations.[14,15,17] In RED systems, the two sides of a membrane in the stack are exposed to different salt concentrations.[1,3,4] Thus, the membrane resistance under these conditions will be much different from those anticipated from resistance measurements at a single high salt concentration. The influence of two different salt concentrations on membrane resistance has not been previously investigated.

We examined ionic resistances of state-of-the-art commercially available ion exchange membranes (Selemion CMV and AMV) equilibrated under conditions where there is a single salt solution and where solutions of different salt concentrations are on either side of the membrane. The difference is important for optimizing and properly modeling membranes, accounting for all of the resistances in RED systems, and modeling realistic upper limits on peak power production from RED. We validated our resistance measurement, made with a concentration difference across the membrane, by comparing calculated RED stack resistance, determined using the individual component resistances via an equivalent series

resistance model, to experimentally measured RED stack resistance. We used two different solutions that are of general interest for RED applications: NaCl, as a substitute for salt in seawater and freshwater, and ammonium bicarbonate (AmB), as this chemical is being explored in applications for converting waste heat into salinity gradients using conventional distillation techniques at relatively low temperatures (~50 °C).[1−3,18]

MATERIALS AND METHODS

Ionic resistance of commercially available Selemion CMV and AMV membranes was measured using a DC measurement technique (see also the Supporting Information).[16,19] Measurements were made while the membranes separated solutions of sodium chloride (NaCl) or ammonium bicarbonate (AmB). The membranes were equilibrated in the solution for at least 24 h prior to the measurement of ionic resistance.

Measuring membrane area resistance when a concentration difference exists across the film requires additional steps compared to the measurement made without a concentration difference (see also the Supporting Information). The membrane must first be equilibrated between the two well-mixed solutions using a flow-through system to allow the membrane to equilibrate between the two solutions without an appreciable change in the solution concentrations during flow-through equilibration. During the resistance measurement, the volumes of the salt solution chambers must be large enough compared to the membrane area and salt permeability of the membrane to ensure that the salt concentrations on either side of the membrane do not change appreciably (i.e., the system is in a pseudosteady state) during the measurement. With a membrane area of 11.4 cm^2, we found that solution volumes of 32 mL on either side of the membrane satisfied this condition for the Selemion membranes. During flow-through equilibration, we used 58 mL chambers on either side of the membrane with a flow rate of 3 mL/min (see also the Supporting Information).

A three-membrane RED stack was prepared using the Selemion CMV and AMV membranes (see also the Supporting Information). Electrolytes were pumped through the stack at a rate of 15 mL/min to mitigate hydrodynamic boundary layer effects. The stack resistance, R_{stack}, was determined by linear regression of the stack potential, measured using Ag/AgCl reference electrodes placed on either side of the stack, versus the current density passed through the stack.[20]

The calculated stack ionic resistance, $R_{stack,calc}$, was determined using the area resistances of the individual stack components, r_i, and an equivalent series resistance model:

$$R_{stack,calc} = \frac{1}{A_m}(r_{cathode} + r_{CEM1|1} + r_{HC} + r_{AEM0.01|1} + r_{LC}$$
$$+ r_{CEM0.01|1} + r_{anode}) \qquad (1)$$

where A_m is the effective membrane area available for charge transport (6.8 cm^2) that was corrected for the spacer shadow effect[3] by subtracting the projected area of the spacers (1.2 cm^2) used to separate the membranes from the maximal membrane area available for charge transport (8 cm^2). The area resistance values for the cathode, high-concentration (HC), low-concentration (LC), and anode chambers were determined from the resistivity of those solutions and the geometry of the RED stack (see also the Supporting Information). The value of $r_{CEM1|1}$ was determined experimentally with 1 mol/L NaCl solutions on both sides of the membranes, and the values of

$r_{CEM0.01|1}$ and $r_{AEM0.01|1}$ were determined experimentally with 0.01 mol/L NaCl on one side and 1 mol/L NaCl on the other side of the membrane, as described above. The cathode and anode chambers were filled with a 1 mol/L salt solution, and the salt solution flowed through the HC (1.0 mol/L) and LC (0.01 mol/L) chambers at a rate of 15 mL/min.

RESULTS AND DISCUSSION

Membrane Resistance with a Single Salt Concentration. The area resistance of the Selemion CMV membrane substantially increased inversely with the NaCl concentration (Figure 1). This trend in resistance as a function of salt
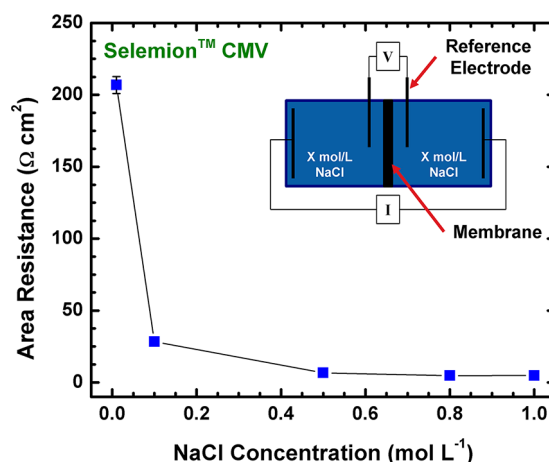

Figure 1. Area resistance as a function of salt concentration for the Selemion CMV membrane. No salt concentration difference existed across the membrane when these resistances were measured, as illustrated in the experimental diagram.

concentration is consistent with results obtained using other membranes,[14,15] and it is consistent with the relationship between aqueous salt solution resistivities and salt concentration.[21] Similar relationships for other membranes have been ascribed to both intrinsic or nonhydrodynamic diffusion boundary layer resistance[14] and changes in the concentration of absorbed and mobile ions[16] in the membrane.

Membrane Resistance with a Salt Concentration Difference. The presence of a salt concentration difference across the membrane increased the area resistance of the membrane dramatically compared to the value measured using the high-concentration solution (Figure 2). The area resistance measured for the Selemion CMV separating 1.0 and 0.01 mol/L NaCl (CEM$_{0.01|1}$) was more than 15 times greater than that measured with 1.0 mol/L NaCl on both sides of the membrane (CEM$_{1|1}$). The area resistance of the Selemion AMV membrane separating 1.0 and 0.01 mol/L NaCl (AEM$_{0.01|1}$ in Figure 2) was more than 13 times greater than that measured with 1.0 mol/L NaCl on both sides of the membrane (3.7 ± 0.1 Ω cm^2). The differences in the area resistance of the membranes measured in NaCl solutions, relative to those in AmB, were consistent with differences in the sizes and dilute solution mobilities of the charge-carrying ions.[11]

The area resistance measurements (Figure 2) were validated using a laboratory-scale RED stack made of CMV and AMV membranes. The calculated stack resistance, $R_{stack,calc}$, was indistinguishable with respect to experimental uncertainty from the stack resistance, R_{stack}, that was measured directly using the RED stack (Figure 3). No adjustable parameters were used in
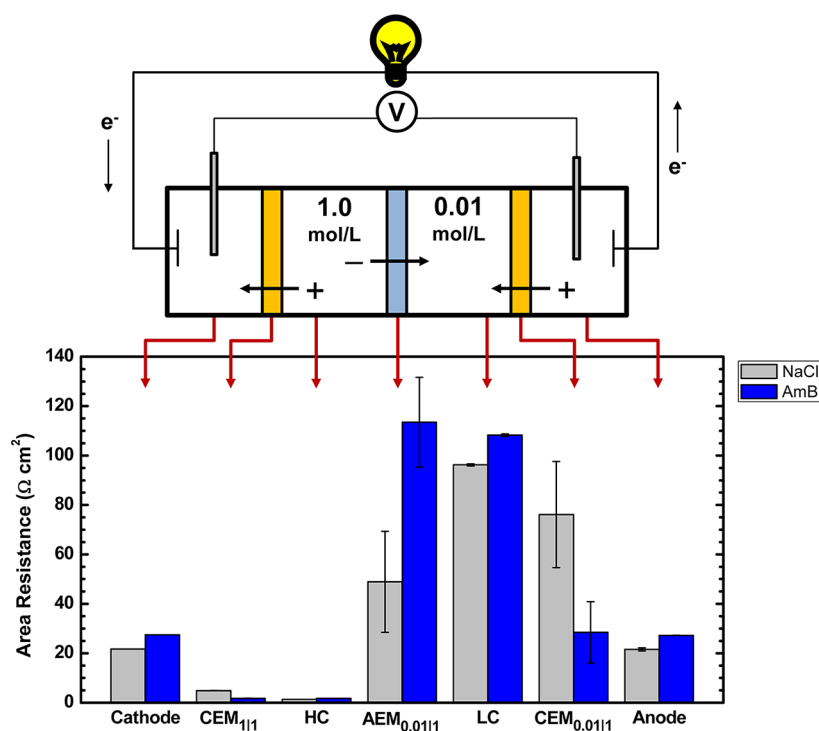
Figure 2. Area resistance values measured (membranes) or calculated [solutions (see the Supporting Information)] individually for each component of the RED stack. Measurements were made using either sodium chloride or ammonium bicarbonate solutions. The concentrations of the catholyte and anolyte solutions were 1 mol/L.
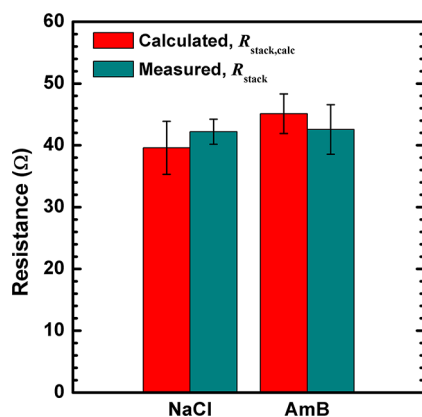

Figure 3. Stack resistance values calculated using eq 1 and data in Figure 2, compared to the stack resistance values measured experimentally using the RED stack. Uncertainty in the calculated values was determined by propagation of the uncertainty values in each of the terms of eq 1, and the uncertainty in the measured stack resistance was determined as one standard deviation from the average of three measured stack resistance values.

the calculation of the stack resistance. The agreement between the calculated (using eq 1; see also the Supporting Information) and experimentally measured stack resistances validates the membrane area resistance measurements made on each membrane individually using the concentration difference method, which may have been a critical missing piece of information in other RED stack resistance models.

The high resistivity of the low-concentration solution (LC in Figure 2) contributed significantly to the overall resistance of the RED stack,[3,22] accounting for 36% (NaCl) or 35% (AmB) of the total resistance in our stack measurements. The area resistances of the ion exchange membranes positioned between

LC and HC solutions (i.e., $AEM_{0.01|1}$ and $CEM_{0.01|1}$ in Figure 2) accounted for 46% (NaCl or AmB) of the overall RED stack resistance. The LC chamber thickness in our RED stack was relatively large (1.13 mm) compared to those of other RED systems.[22] Therefore, a more optimized LC chamber could greatly reduce the LC area resistance but would not appreciably decrease the area resistance of the ion exchange membranes. For example, if the resistance of the LC chamber was reduced by a factor of 10, which may be reasonable with a 100 μm spacer,[23] the contribution of $AEM_{0.01|1}$ and $CEM_{0.01|1}$ to the overall stack resistance would increase to 68% (NaCl) or 67% (AmB). In RED stacks with well-designed hydrodynamics and low LC chamber resistances, the membrane resistances across compartments with unequal salt concentrations may be the dominant factor in determining system performance. As long as the concentration difference remains, the issue of membrane resistance will likely exist and may need to be addressed through further fundamental studies of ion transport in polymers and membrane engineering (e.g., thinner membranes could help mitigate these resistances[9]).

Increases in the ionic resistance of other membranes as salt concentration decreases (similar to the data in Figure 1) have been ascribed to concentration polarization or diffusion boundary layer resistance.[5,14] The flow rates of the HC and LC feeds to our RED stack were 15 mL/min. Above this flow rate, the resistance of the stack did not change appreciably, suggesting that hydrodynamic diffusion boundary layer resistance largely had been mitigated. The current densities used in the stack measurements were similar to the current densities used in the membrane resistance measurements made using the salt concentration difference, so it is possible that some diffusion boundary layer resistance is inherent to the resistance measurement. Nevertheless, these experiments suggest that these boundary layer resistances may be inherent

to the passage of current through the membrane and not particularly affected by the hydrodynamics of the RED stack.

The high resistance of membranes separating salt solutions of different concentrations relative to the resistance of membranes in a concentrated salt solution is detrimental to the ability of a RED system to efficiently produce clean, renewable energy. In our measurements, the resistance of membranes that separate salt solutions of different concentrations was comparable to the resistance of the LC solutions in the RED stack. These results highlight a need for modeling efforts to understand the fundamental underpinnings of such phenomena. Membrane models will need to be structured to account for the highly nonlinear dependence of membrane resistance on salt concentration that is shown in Figure 1. This insight into membrane resistance under operating conditions further highlights the need to develop improved low-resistance membranes for RED and to understand intrinsic ion transport phenomena in polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information regarding area resistance measurement techniques, reverse electrodialysis stack experimental details, and solution resistance calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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