Ammonium Bicarbonate Transport in Anion Exchange Membranes for Salinity Gradient Energy

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S *Supporting Information*

ABSTRACT: Many salinity gradient energy technologies such as reverse electrodialysis (RED) rely on highly selective anion transport through polymeric anion exchange membranes. While there is considerable interest in using thermolytic solutions such as ammonium bicarbonate (AmB) in RED processes for closed-loop conversion of heat energy to electricity, little is known about membrane performance in this electrolyte. The resistances of two commercially available

cation exchange membranes in AmB were lower than their resistances in NaCl. However, the resistances of commercially available anion exchange membranes (AEMs) were much larger in AmB than in NaCl, which would adversely affect energy recovery. The properties of a series of quaternary ammonium-functionalized poly(phenylene oxide) and Radel-based AEMs were therefore examined to understand the reasons for increased resistance in AmB to overcome this performance penalty due to the lower mobility of bicarbonate, 4.59×10^{-4} cm^2/(V s), compared to chloride, 7.90×10^{-4} cm^2/(V s) (the dilute aqueous solution mobility ratio of HCO$_3^-$ to Cl$^-$ is 0.58). Most membrane resistances were generally consistent with the dilute solution mobilities of the anions. For a few key samples, however, increased water uptake in AmB solution reduced the ionic resistance of the polymer compared to its resistance in NaCl solution. This increased water uptake was attributed to the greater hydration of the bicarbonate ion compared to the chloride ion. The increased resistance due to the use of bicarbonate as opposed to chloride ions in AEMs can therefore be mitigated by designing polymers that swell more in AmB compared to NaCl solutions, enabling more efficient energy recovery using AmB thermolytic solutions in RED.
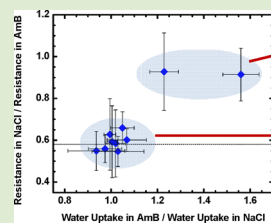
Recent interest in salinity gradient energy technologies to address global energy needs, such as reverse electro-dialysis[1–4] (RED), capacitive energy extraction based on Donnan potential[5] (CDP), and capacitive reverse electro-dialysis[6] (CRED), has encouraged the study of ion-containing polymers to optimize ion exchange membranes for these processes.[4,7,8] These technologies rely on membranes that are capable of selectively transporting ions under the influence of an electric field.[7,8] The ionic resistance of the membranes in these processes is a critical parameter as large resistances reduce the energy efficiency of the devices.[1,2,9,10] Many researchers have reported the ionic resistance of polymers measured using aqueous NaCl[1,11] because sodium and chloride are the predominant ions in many natural water sources.[12] Thermolytic salts, such as aqueous ammonium bicarbonate (AmB), are being considered for salinity gradient energy production because these solutions permit closed-loop conversion of heat energy to electricity.[4,13,14] Little is known, however, about AmB transport in different types of polymer membranes. The ionic resistance of ion-containing polymers measured using NaCl solutions may not be representative of the ionic resistance of those materials in AmB electrolytes.

The efficiency of AmB-based technologies, such as RED for waste heat recovery, critically depends on controlling rates of ammonium and bicarbonate transport through ion-containing polymers. To demonstrate that ion transport was different for

membranes in AmB versus NaCl electrolytes, we measured the ionic area resistance of two commercially available cation exchange membranes (CEMs) and two commercially available anion exchange membranes (AEMs) using these two salts (Figure 1). The area resistances of the AEMs in AmB were greater than those in NaCl. As a result, switching from NaCl to AmB in a RED device could reduce energy efficiency even though the area resistance of the CEMs in AmB is less than that in NaCl. AEMs that do not have substantially increased ionic resistance with AmB compared to NaCl (i.e., AEMs that behave differently from those commercial AEMs shown in Figure 1) are desirable for use in AmB-based salinity gradient technologies such as RED to overcome the differences in membrane resistance based on the properties of the electrolyte.

The differences in resistance measured using the two electrolytes reported in Figure 1 can be rationalized, to a first approximation, as resulting from differences in the dilute solution mobilities of ammonium and bicarbonate ions compared to sodium and chloride ions. The dilute solution mobilities of NH$_4^+$ and Na$^+$ are 7.71×10^{-4} cm^2/(V s) and 5.18×10^{-4} cm^2/(V s), respectively, so for a CEM that transports
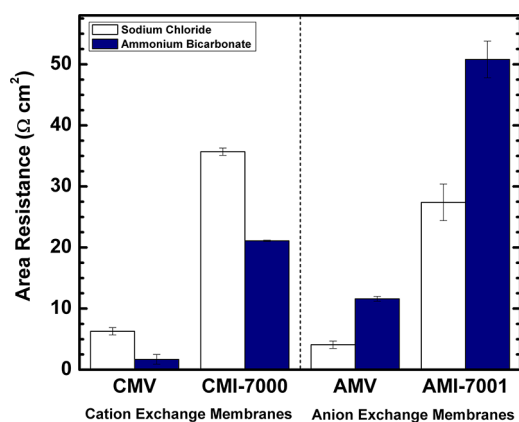
Figure 1. Area resistance at room temperature of commercially available ion exchange membranes (Selemion CMV and AMV and Membranes International, Inc. CMI-7000 and AMI-7001) measured using either 0.5 mol/L NaCl or AmB solutions.

Figure 2. Structures of the anion exchange polymers, which are shown in their "as-prepared" counterion form, considered in this study.

predominantly cations the resistance ratio of sodium chloride to ammonium bicarbonate $(r_{m,NaCl}/r_{m,AmB})$ might be expected to be 1.49, i.e., the mobility ratio of NH_4^+ to Na^+.[15] This ratio is favorable for AmB-based RED because the resistance of the CEM is lower in AmB compared to NaCl. The dilute solution mobilities of HCO_3^- and Cl^- are 4.59×10^{-4} and 7.90×10^{-4} cm^2/(V s), respectively, so for an AEM that transports predominantly anions the resistance ratio of sodium chloride to ammonium bicarbonate $(r_{m,NaCl}/r_{m,AmB})$ might be expected to be 0.58, i.e., the mobility ratio of HCO_3^- to Cl^-, which is unfavorable for AmB-based RED because the predicted resistance of the AEM is greater in AmB compared to NaCl.[15]

The ratios of the resistances of the commercial membranes in NaCl to that in AmB (Figure 1), which can be compared to the values calculated from dilute solution mobility, are 3.7 ± 1.8 (CMV), 1.7 ± 0.1 (CMI-7000), 0.35 ± 0.05 (AMV), and 0.54 ± 0.07 (AMI-7001). The approximate agreement between the ratios of the resistance data presented in Figure 1 and the ratios of the dilute solution mobilities is reasonable given that these commercial membranes are reinforced using a nonconductive material and do not have greatly different water uptake in either electrolyte solution.

To understand how to reduce the ionic resistance of AmB in AEMs, we investigated the properties of a range of candidate materials as alternatives to the commercial membranes. A key difference between the commercial samples and our experimental samples was that our membranes were not mechanically restricted by the presence of a reinforcing material. Exposing a nonreinforced polymer to a bicarbonate-containing salt can swell the polymer to a greater extent than would occur in a chloride-containing salt because bicarbonate ions are more highly hydrated than chloride ions.[16] Because membranes that absorb more water generally have lower resistance, we wanted to take advantage of this swelling phenomenon to decrease the resistance of the membrane when exposed to the low mobility bicarbonate-containing electrolyte. The polymers selected for the experimental AEMs had aromatic backbones with various levels of quaternary ammonium functionality (Figure 2). Synthesis details for quaternary ammonium functionalized poly(sulfone) (aRadel[17]) and quaternary ammonium functionalized poly(phenylene oxide) (aPPO[18]) have been reported previously. Additional details about the polymers, film casting,
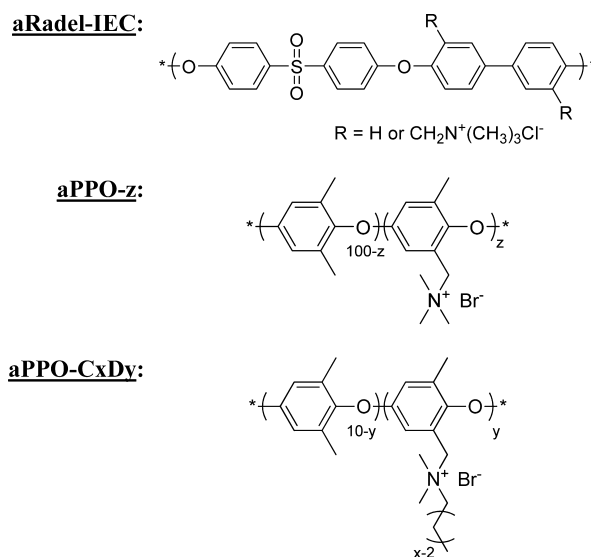
and pre-experiment conditioning procedures are provided as Supporting Information.

Ionic resistance was measured using a direct current (DC) method[19] described in the Supporting Information. For the AEMs shown in Figure 2, we report the thickness-normalized intrinsic resistance (in units of Ω m) because thickness can have a profound effect on a polymer's area resistance (in units of Ω cm^2, used in Figure 1), and as noted, the commercial membranes have a heterogeneous reinforced structure that prevents accurate calculation of intrinsic resistance.[9] Data were reported as averages of at least three measurements, and standard error propagation[20] was used to estimate experimental uncertainty based on the standard deviations of the ionic resistance and thickness measurements.

The intrinsic resistance of several aRadel and aPPO polymers (Figure 3) was greater in AmB $(r_{m,AmB})$ than NaCl $(r_{m,NaCl})$,
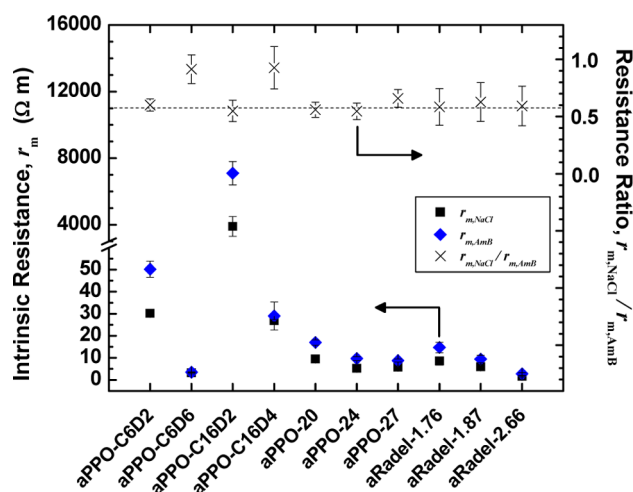

Figure 3. Intrinsic resistance values for aPPO and aRadel measured in 0.5 mol/L sodium chloride or ammonium bicarbonate. The ratio of the intrinsic resistance measured in sodium chloride to that measured in ammonium bicarbonate is indicated on the plot for each polymer, and the dashed line represents the calculated ratio of the bicarbonate dilute solution mobility to that of chloride.

similar to that obtained with the commercial AEMs (Figure 1). The resistance ratios ($r_{m,NaCl}/r_{m,AmB}$) for all but two of the samples were consistent with the value of 0.58 that was calculated from the dilute solution anion mobilities. These results further demonstrated that ion transport was primarily, but not always, limited by the dilute solution mobilities of the mobile ions in these polymers. Two notable exceptions to this correlation of membrane resistance and ion mobility were the aPPO-C6D6 and aPPO-C16D4 polymers. In these two cases, the resistance ratio was much higher than that obtained for the other polymers in AmB and higher than the dilute solution mobility ratio. This result suggested that it was possible to prepare membranes that did not strictly adhere to the dilute solution mobility ratio constraint when moving from NaCl to the AmB electrolyte.

The observation that the relative rates of ion transport in these polymers are, in many cases, described by the dilute solution mobility ratios likely reflects the sensitivity of ion transport to hydrated ion size. Chemically driven salt transport in water-swollen uncharged poly(ethylene glycol) hydrogels is sensitive to ion size in a manner that is consistent with free volume theory when free volume is taken to be proportional to the water content of the films.[21] The relative rates of ion transport in many of the AEMs considered in this study, which have water uptake values ranging from 0.15 to 0.56 g(water) g^{-1}(dry polymer), do not appear to vary with water content in the manner predicted by free volume theory. This result suggests that further study is needed to understand the similarities and/or differences between chemically and potential field-driven ion transport experiments across different classes of materials and to relate ion transport to the physics of ions in solution and classical theories of small-molecule transport in polymers.

The anomalous resistance behavior of aPPO-C6D6 and aPPO-C16D4 was due to the different water uptake properties of these polymers in AmB and NaCl electrolytes compared to the other materials (Figure 4). The resistance ratios ($r_{m,NaCl}/r_{m,AmB}$) for all polymers except these two samples cluster around a water uptake ratio of approximately 1, resulting in the expected intrinsic resistance ratio of 0.58. This result shows that
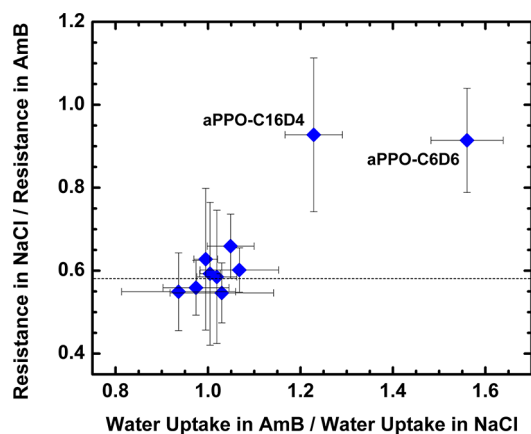

Figure 4. Intrinsic resistance measured using 0.5 mol/L sodium chloride divided by that measured using 0.5 mol/L ammonium bicarbonate versus the ratio of water uptake in 0.5 mol/L AmB to that in 0.5 mol/L NaCl. The dashed line represents the ratio of the bicarbonate dilute solution mobility to that of chloride, which is equal to 0.58.

when polymers have the same water uptake in each electrolyte their resistances are consistent with the dilute solution mobility of the mobile ion. The resistance ratios of the aPPO-C6D6 and aPPO-C16D4 samples were consistent with their much greater water uptake in AmB than NaCl, resulting in greater membrane swelling. Water uptake data for the commercial membranes (Figure 1) equilibrated in 0.5 mol/L NaCl and AmB are reported and discussed as Supporting Information.

Increasing the water uptake of a polymer generally facilitates ion transport,[7,8,21,22] and in this case, higher water uptake resulted in lower ionic resistance (i.e., higher conductivity). For aPPO-C6D6 and aPPO-C16D4, greater water uptake in 0.5 mol/L AmB compared to NaCl lowered the resistance of the polymer measured using AmB, thereby resulting in a $r_{m,NaCl}/r_{m,AmB}$ ratio above the value predicted using dilute solution mobilities (i.e., above the dashed line in Figures 2 and 3).

Increased water uptake in a polymer in AmB compared to NaCl could be related to the activity of water in these two electrolytes. Equations of state, such as Flory–Huggins theory,[23,24] predict that the volume fraction of water sorbed in (and, thus, the water uptake of) a polymer will be higher when the polymer is exposed to a higher activity of water. As such, one might expect that the water uptake of a polymer would be greater in AmB compared to NaCl based on the slightly higher activity of water of 0.985 in 0.5 mol/L AmB (determined using OLIAnalyzer) compared to 0.984 for 0.5 mol/L NaCl. According to Flory–Huggins theory (see also Supporting Information), this small difference in water activity would produce <1% change in the water sorption of a representative polymer. Thus, for aPPO-C6D6 and aPPO-C16D4, the difference between the thermodynamic activities of water does not appear to explain the water uptake data in Figure 4.

The nature of the counterions provides insight into the water uptake behavior. Bicarbonate is a more kosmotropic ion than chloride according to the Hofmeister series, meaning that bicarbonate is more highly hydrated than chloride.[16] Both aPPO-C6D6 and aPPO-C16D4 are relatively highly functionalized, based on ion exchange capacities of 2.89 and 1.68 meq/g (dry polymer), respectively, compared to the other polymers (see also Supporting Information). Ion exchange from the chloride to the bicarbonate counterion form introduces additional water into these polymers because the bicarbonate ions effectively make the polymer more hydrophilic and bring more water into the polymer matrix compared to the chloride ions. These effects may be more significant in highly functionalized polymers because the concentration of counterions, e.g., anions in AEMs, in such materials is greater than that in less functionalized polymers.

The aRadel-2.66 polymer is also highly functionalized, but the water uptake of this polymer in 0.5 mol/L AmB is statistically indistinguishable from that in 0.5 mol/L NaCl. This difference between the aPPO and aRadel polymers may be related to morphology. The highly functionalized aPPO polymers contain alkyl side chains that can drive molecular-scale order.[18,25] Indeed, liquid D$_2$O swollen aPPO-C16D4 exhibits nanophase separation, as detected using small-angle neutron scattering (SANS) and reported in Figure 5, while aRadel does not.

Nanophase separation in aPPO-C16D4 will increase the local ion concentration of the polymer thereby making it behave as though it were more highly functionalized than a nonphase-separated polymer at a similar overall IEC. While SANS data
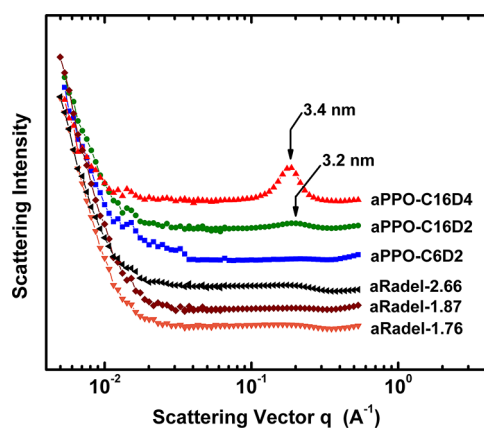
Figure 5. Small-angle neutron scattering (SANS) results for aPPO-CxDy and aRadel. Films were equilibrated in liquid D_2O at ambient temperature and pressure during the SANS measurement, and primary feature spacings are listed for aPPO-C16D2 and aPPO-C16D4.

for aPPO-C6D6 were not available, aPPO-C6D2 does not appear to nanophase separate, but aPPO-C16D2 does nanophase separate (Figure 5) suggesting that it is possible that aPPO-C6D6, which contains three times the number of side chain functional groups as aPPO-C6D2, may be nanophase separated. Increased fixed charge group concentration (i.e., increased local IEC) due to nanophase separation could amplify the ion-specific hydration effects described previously, thereby resulting in polymers that sorb more water in 0.5 mol/L AmB compared to NaCl.

These results demonstrate that ammonium transport is favorable in commercially available CEMs compared to sodium transport but that bicarbonate ion transport in many AEMs is primarily hindered by the lower ion mobility of bicarbonate compared to chloride. Ionic resistance of many ion exchange membranes measured using NaCl and AmB tends to follow predictions based on the dilute solution mobilities of the charge carrying ions. In materials that show this relationship, the water uptake does not change greatly when the polymer is exposed to different electrolyte solutions.

By controlling membrane swelling properties, we showed that it was possible to prepare AEMs that have ionic resistances in AmB that are closer to those measured using NaCl to overcome the dilute solution mobility limits of bicarbonate and chloride, the majority charge carriers in AEMs. Such materials will need to be able to swell freely so that the water uptake of the polymer in 0.5 mol/L AmB can be greater than that in 0.5 mol/L NaCl. This difference in water uptake, which occurs because the bicarbonate ions effectively carry more water into the membrane to increase its swelling, drives ionic resistance values measured in AmB to be lower than that predicted from values calculated using the dilute solution mobilities and ionic resistance data for the polymer measured using NaCl. These effects were most profound in polymers that were highly functionalized and/or nanophase separated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Additional information regarding the preparation and characteristics of the polymer films, experimental method information, discussion of commercial membrane water uptake data and discussion of Flory−Huggins 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.

■ ACKNOWLEDGMENTS

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