Ionic Resistance and Permselectivity Tradeoffs in Anion Exchange Membranes

Geoffrey M. Geise,[†,‡] Michael A. Hickner,*,[†] and Bruce E. Logan[‡]

[†]Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
[‡]Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

ABSTRACT: Salinity gradient energy technologies, such as reverse electrodialysis (RED) and capacitive mixing based on Donnan potential (Capmix CDP), could help address the global need for noncarbon-based energy. Anion exchange membranes (AEMs) are a key component in these systems, and improved AEMs are needed in order to optimize and extend salinity gradient energy technologies. We measured ionic resistance and permselectivity properties of quaternary ammonium-functionalized AEMs based on poly(sulfone) and poly(phenylene oxide) polymer backbones and developed structure−property relationships between the transport

properties and the water content and fixed charge concentration of the membranes. Ion transport and ion exclusion properties depend on the volume fraction of water in the polymer membrane, and the chemical nature of the polymer itself can influence fine-tuning of the transport properties to obtain membranes with other useful properties, such as chemical and dimensional stability. The ionic resistance of the AEMs considered in this study decreased by more than 3 orders of magnitude (i.e., from 3900 to 1.6 Ω m) and the permselectivity decreased by 6% (i.e., from 0.91 to 0.85) as the volume fraction of water in the polymer was varied by a factor of 3.8 (i.e., from 0.1 to 0.38). Water content was used to rationalize a tradeoff relationship between the permselectivity and ionic resistance of these AEMs whereby polymers with higher water content tend to have lower ionic resistance and lower permselectivity. The correlation of ion transport properties with water volume fraction and fixed charge concentration is discussed with emphasis on the importance of considering water volume fraction when interpreting ion transport data.

KEYWORDS: ion transport, water uptake, polymer swelling, ion exchange membrane, quaternary ammonium polymer
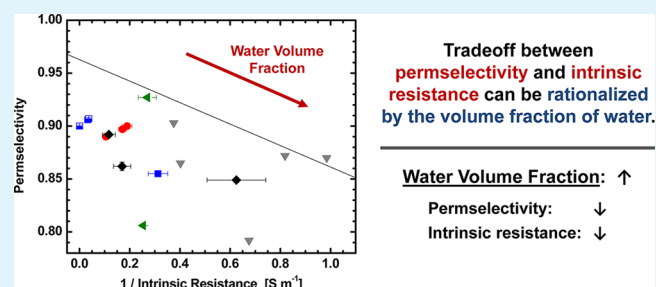
1. INTRODUCTION

Providing sufficient and sustainable supplies of energy and water is a key challenge facing society.[1−7] Salinity gradient technologies, such as reverse electrodialysis (RED)[8−11] and capacitive mixing based on Donnan potential (Capmix CDP),[12] in addition to water purification processes, such as electrodialysis (ED)[13,14] and membrane capacitive deionization (MCDI),[15,16] could help address the global need for supplies of energy and water. In many cases, further optimization of these technologies is needed to improve their effectiveness for energy and water applications. A significant amount of work has been performed to address configuration and engineering of these systems in terms of optimization of unit operations, flow distribution in the stacks, and economics, but it is recognized that improved membrane materials have a role to play in promoting widespread commercialization of salinity gradient energy technologies.[8]

In these aqueous processes, ion containing polymers are used as cation exchange membranes (CEMs), anion exchange membranes (AEMs), or electrode coatings to control relative rates of ion transport.[17] The key ion transport properties of these polymers for potential field-driven applications are ionic

resistance and permselectivity, which characterize, respectively, the tendency of a polymer to resist the passage of ionic current and the ability of the polymer to transport only counterions (i.e., cations in CEMs or anions in AEMs) and exclude co-ions (i.e., anions in CEMs or cations in AEMs).[17−19] Both properties are inherently sensitive to the chemical structure of the polymer, but systematic structure−property guidelines, particularly for AEMs and permselectivity, are scarce.[20−27]

Water uptake, or more precisely water volume fraction, is a key property that affects ion transport in water-swollen polymers.[5,7,28,29] In addition to polymer backbone structure, molecular weight, and cross-link density, water volume fraction can be modulated by adjusting the degree of fixed charge functionalization, i.e., the gravimetric ion exchange capacity (IEC) of the polymer in units of mequiv/g (dry polymer), and increasing the IEC generally increases the water uptake of a polymer.[7,28] While IEC is a useful metric for characterizing polymer structure, it does not reflect the ion concentration of

the water-swollen polymer.[29] Fixed charge concentration, C_A, is more useful in this regard because C_A is determined by both the IEC and water uptake of the polymer.[5,29,30] One of the challenges in comparing structure−property studies of membranes in the literature is inconsistency in the parameters (particularly those relating to the fixed charge group content of the polymer) used to characterize the polymers. We adopt the definition of fixed charge concentration, in units of mequiv cm^{-3} (swollen polymer), recommended by Helfferich for treatment of transport data, which is equivalent to molar concentrations in mol L^{-1} (swollen polymer).[31] Both the fixed charge concentration and the water content of the polymer should be considered when interpreting ionic resistance and permselectivity properties of anion exchange membranes.

Ionic resistance is generally sensitive to the fixed charge concentration of the polymer and often decreases as C_A and water volume fraction increases.[9] In single ion conductors that do not contain any appreciable mobile salt, the relationship between ionic resistance and fixed charge concentration is, to a first approximation, reasonably straightforward at moderate water contents because increasing the fixed charge concentration of the polymer introduces more charge carriers (i.e., mobile ions) into the polymer, thereby decreasing the ionic resistance (i.e., increasing the conductivity) of the polymer.[32] The polymers considered in this study, however, are hydrated with aqueous salt solutions, so these materials contain some mobile salt that could also carry ionic current through the polymer in addition to the mobile counterions native to the membrane.[29,33] At a given external salt solution concentration, the concentration of mobile salt in these polymers and the mobility of the ions in the polymer are expected to be sensitive to the water content of the polymer that, in turn, is related to the fixed charge concentration.[28,33,34] Therefore, we discuss ionic resistance with respect to both the water content and fixed charge concentration of the polymers.

The ionic resistance of commercially available ion exchange membranes is often reported as area resistance because this quantity is useful for predicting the performance of the membrane in many applications, and the thickness of the membrane is essentially fixed by the manufacturing process.[9,10,17,35] Simply decreasing the thickness of a polymer film tends to reduce area resistance,[20] which frustrates evaluation and comparison of the intrinsic ion transport properties of polymer films prepared at different film thicknesses. For homogeneous polymer films, such as the membranes considered in this study, area resistance can be normalized by film thickness to obtain the intrinsic ionic resistance (i.e., resistivity) of the polymer.[18,19] The intrinsic ionic resistance accounts for different thicknesses between samples and allows for direct comparison of the intrinsic ion transport properties of different polymers.

Permselectivity describes the ability of the polymer to pass current solely by means of the counterions (i.e., ions with charges opposite to those that are bound to the polymer backbone) in the polymer.[18] Thus, a perfectly permselective membrane is one where co-ions (i.e., the ions with the same charge as those that are bound to the polymer backbone) are completely excluded from the polymer matrix and prevented from migrating through the membrane.[17,29] For AEMs, such a perfectly permselective membrane would transport current only via anionic charge carriers since all cations would be excluded from the material.[17] If co-ion transport occurs (i.e., cations are

not completely excluded from the polymer), the permselectivity will decrease below the perfectly permselective value of 1.[17−20]

High fixed charge concentration is generally considered to be desirable for producing highly permselective ion exchange membranes[9,17,18,20] because electrostatic exclusion of co-ions increases as fixed charge concentration increases according to Donnan theory.[29] The influence of Donnan exclusion on permselectivity can be demonstrated using permselectivity measurements made as a function of salt concentration. Decreases in AEM permselectivity with increasing salt concentration[26,27] suggest that Donnan exclusion of co-ions, which is more effective at low salt concentration,[29] increases permselectivity.

Polymer water content (i.e., swelling) generally decreases with increasing solution salt concentration (i.e., osmotic deswelling).[26,33,36,37] Therefore, the observation that AEM permselectivity decreases with increasing salt concentration and a simultaneous increase in fixed charge concentration (because the water content of the polymer decreases with osmotic deswelling)[26,27] suggests that the effects of solution salt concentration on Donnan exclusion may influence permselectivity more significantly than the water-swollen membrane fixed charge concentration. This result suggests that, while high fixed charge concentration in the membrane may generally be viewed as desirable for producing highly permselective polymers, other variables that affect Donnan exclusion (e.g., salt concentration[29,33] and water content[33]) may also influence permselectivity.

Permselectivity was reported to increase with increasing fixed charge content of the polymer for cross-linked polymers based on methacrylate[21,25] and epichlorohydrin[20] monomers. In the case of the methacrylate-based[21,25] polymers, permselectivity increased with increasing water uptake, but permselectivity of the epichlorohydrin-based[20] polymers decreased as water uptake increased. Additionally, the permselectivity of diamine cross-linked chloromethylated polysulfones was reported to increase with increasing fixed charge content when the diamine cross-linker contains 3 or fewer methylene groups between the two amines (i.e., N,N,N′,N′-tetramethylethylenediamine or N,N,N′,N′-tetramethyl-1,3-propanediamine) and increasing water uptake.[23] These results are consistent with the general view that permselectivity increases with increasing fixed charge concentration, even though fixed charge concentration, defined as mequiv per volume of swollen polymer, was reported only for the methacrylate-based[21,25] AEMs.

The permselectivity of some polymers, however, appears to decrease with increasing fixed charge content opposite to the trends in the studies discussed above. Examples of such polymers are diamine cross-linked chloromethylated poly-(sulfone)s (where the diamine contains more than 3 methylene units between the amine end groups)[23,24] and DABCO cross-linked poly(styrene)[22] AEMs. In all of these polymers, permselectivity decreased as water content increased unlike the permselectivity of the methacrylate-based AEMs[21,25] that increased with increasing water content. Unfortunately, the fixed charge concentration of these polymers was not reported and cannot be calculated from the data that are available due to the unknown densities of the samples, but these results suggest that increasing fixed charge concentration does not always increase permselectivity and that both the water volume fraction and fixed charge concentration must be taken into consideration.

The decrease in permselectivity with increased water content for some of the polymers discussed above may be explained by recent salt sorption data for sulfonated polymers.[33] These data suggested that increasing water uptake in high fixed charge concentration polymers may reduce the effectiveness of Donnan exclusion and increase sorption of co-ions as a result of the spatial heterogeneity of the electric field throughout the polymer (i.e., a breakdown in the assumptions of Donnan theory).[33] This result indicates that permselectivity may actually decrease as fixed charge concentration increases if water content increases significantly and the reduction in Donnan exclusion effectiveness discussed above occurs. As a result, we must consider permselectivity with respect to both water content and fixed charge concentration as the nature of the polymer appears to influence the extent to which the material follows ideal Donnan theory assumptions.

While combinations of high permselectivity and low ionic resistance are generally viewed as desirable for ion exchange membranes, not all processes necessarily require the same combinations of permselectivity and ionic resistance. For example, the efficiency of a closed-loop ammonium bicarbonate RED process[8,38] might tolerate moderately permselective and low ionic resistance membranes because co-ion crossover may not be as significant an issue in this closed-loop process since the primary objective is to produce electricity, not perform a separation. A similar situation has been reported for pressure retarded osmosis (PRO) where the goal of the process is also energy generation as opposed to performing a separation.[39] Therefore, it is desirable to understand how to tune, at the fundamental polymer structure level, the ionic resistance and permselectivity of ion containing polymers to access desired combinations of ionic resistance and permselectivity for a given application.

We have characterized the ionic resistance and permselectivity properties of a series of AEMs prepared using aromatic Radel poly(phenylsulfone)[40,41] or poly(2,6-dimethyl-1,4-phenylene oxide)[42,43] backbones (Figure 1). We demonstrate that the ion transport properties of these polymers can be rationalized by the water content of the polymer, and polymer backbone chemistry can be used to further optimize the ion transport properties of the polymer. The observed dependence of ionic resistance and permselectivity on the water content of the polymer provides a basis for understanding a tradeoff relationship between the permselectivity and ionic resistance of these polymers. This relationship is similar to tradeoff relationships between separation performance and transport rate identified in membranes for desalination,[44] ultrafiltration,[45] and gas separation[46,47] applications but adds new insight into the mechanisms governing the performance of ion-containing membranes.

2. EXPERIMENTAL SECTION

2.1. Materials. The AEMs used in this study were prepared from commercially available poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (cat. no. 181781, Aldrich) and Radel (Radel-R-5500 NT, Solvay) backbones. Quaternary ammonium functionalized Radel (aRadel-IEC) polymers (Figure 1) were prepared by reacting chloromethylated Radel with trimethylamine.[40,41] Brominated PPO was reacted with trimethylamine to prepare aPPO-z polymers or a tertiary amine containing two methyl substituents and one alkyl substituent to prepare aPPO-CxDy polymers (Figure 1).[42,43] The sample nomenclature in Figure 1 describes the extent of functionalization for the polymers in terms of IEC for aRadel and degree of functionalization for aPPO and the alkyl side chain length for aPPO-CxDy.

Polymer films were cast in PTFE molds. The aRadel films were solution cast from 5% (w/v) polymer in N,N-dimethylformamide (DMF), and aPPO films were solution cast from 5% (w/v) polymer in 1-methyl-2-pyrrolidinone (NMP). The films were dried at ambient pressure in a gravity oven (VWR Scientific 1330 GM) at either 35 °C (aRadel) or 80 °C (aPPO) for at least 2 days followed by drying under vacuum at the same temperatures for an additional 2 days. Transparent films with thicknesses typically between 70 and 120 μm thick were prepared, and the thickness variation across the area of the films was <10%. Prior to characterization, the films were removed from the PTFE molds and soaked for at least 3 days in deionized (DI) water (18.2 MΩ cm) that was replaced each day. This soaking procedure allowed the films to fully hydrate and extracted any residual casting solvent from the polymer. The ion exchange capacity (IEC) and degree of functionalization (DF) values for the polymers considered in this study are listed in Table 1.

2.2. Methods. *2.2.1. Water Uptake.* Water uptake was determined gravimetrically by first soaking the sample in 0.5 mol/L NaCl solution and rapidly (i.e., within 10 s of removing the sample from the solution) measuring the wet mass, m_{wet}, of the sample after removing excess solution from the surface of the film with an absorbent lab wipe. The sample was dried under vacuum at either 35 °C (aRadel) or 80 °C (aPPO), to avoid degradation of the polymer, in a vented Petri dish[48]
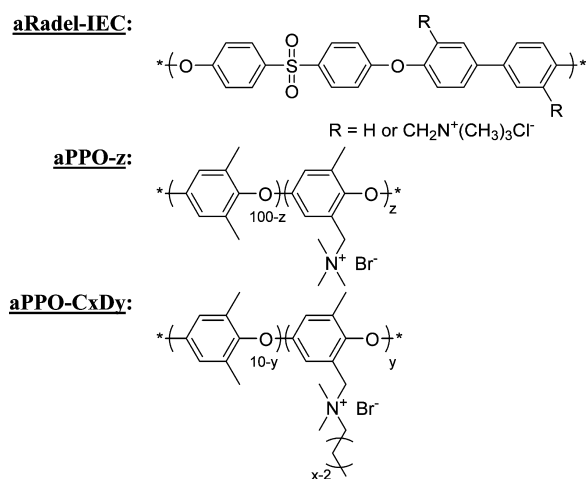
Figure 1. Structures of the aRadel-IEC, aPPO-z, and aPPO-CxDy polymers.

Table 1. Physical Properties of the Polymers Considered in This Study

sample	IEC[a] [mequiv/g(dry polymer)]	DF[a]	dry polymer density [g/cm³]
aRadel-1.76	1.76	0.87	1.13 ± 0.03
aRadel-1.87	1.87	0.94	1.18 ± 0.01
aRadel-2.66	2.66	1.49	1.23 ± 0.02
aPPO-20	1.48	0.20	1.04 ± 0.02
aPPO-24	1.74	0.24	1.02 ± 0.01
aPPO-27	1.93	0.27	1.13 ± 0.04
aPPO-C6D2	1.31	0.20	1.11 ± 0.02
aPPO-C6D6	2.89	0.60	1.13 ± 0.01
aPPO-C16D2	1.08	0.20	1.10 ± 0.01
aPPO-C16D4	1.65	0.40	1.01 ± 0.01

[a]Degree of functionalization (DF) was measured using ¹H NMR and used to calculate the ion exchange capacity (IEC) of the polymer. DF greater than 1 means that more than one fixed charge group is present per repeat unit.

until the dry mass, m_{dry}, of the polymer stabilized. Water uptake, w_u, was calculated as

$$w_u = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{1}$$

Water uptake data are reported as the average of at least four measurements with uncertainty taken as one standard deviation from the mean. After complete drying, the samples were discarded and not used for further analysis.

The volume fraction of water sorbed in the polymer, ϕ_w, was calculated assuming volume additivity:[37]

$$\phi_w = \frac{w_u}{w_u + \rho_w/\rho_p} \tag{2}$$

where ρ_w and ρ_p are the densities of water (taken as 1.0 g cm^{-3})[49] and dry polymer, respectively. The dry polymer density (Table 1) was measured using helium pycnometry[50] at room temperature, and films were dried for at least 2 days under vacuum prior to the measurement. Additionally, the dry polymer density and IEC of the polymer were used to calculate the fixed charge concentration (i.e., the concentration of quaternary ammonium groups per volume of swollen polymer), C_A, assuming volume additivity:[37]

$$C_A = IEC \times \rho_m = \frac{IEC}{(w_u/\rho_w) + (1/\rho_p)} \tag{3}$$

where ρ_m is the mass concentration of polymer per volume of swollen polymer. Finally, the hydration number (i.e., moles of water absorbed in the polymer per equivalent of quaternary ammonium), λ, was calculated as:

$$\lambda = \frac{w_u}{IEC \times MW_w} \tag{4}$$

where MW_w is the molar mass of water (18 g mol^{-1}).

2.2.2. Intrinsic Ionic Resistance. Intrinsic ionic resistance was measured using a DC current method.[19] The sample was soaked in aqueous 0.5 mol/L NaCl for at least 24 h prior to the measurement to ensure that the film equilibrated with the salt solution. A custom-built membrane-separated cell was used to hold the film between two reservoirs that were filled with 0.5 mol/L NaCl. Platinum mesh electrodes that spanned the cross-sectional area of the cell were fixed on both ends of the cell, and Ag/AgCl reference electrodes (RE-5B, BASi, West Lafayette, IN) were positioned on either side of the film. The position of the reference electrodes remained constant throughout the entire experiment. DC current was passed between the Pt electrodes, and the reference electrodes were used to measure the electric potential drop across the film. The potential across the reference electrodes was recorded as a function of current density (typically 40−900 mA cm^{-2}) both when the film sample was loaded in the cell and without a film loaded in the cell. Area resistance was determined by linear regression of the potential difference versus current density data. The measurement made without a film loaded in the cell was used to measure the background resistance of the cell, and this value was subtracted from the measurement made with the film clamped in the cell to obtain the area resistance of the sample. Intrinsic ionic resistance, $r_{m,i}$, was calculated from the area resistance, $r_{m,A,i}$, by normalizing the area resistance by the thickness, l, of the film:[19]

$$r_{m,i} = \frac{r_{m,A,i}}{l} \tag{5}$$

The hydrated film thickness was measured immediately after the resistance measurement using a digital micrometer (Mitutoyo Series 293−344, Aurora, IL), and several measurements were made over the area of the film to determine the uniformity of the film thickness.

2.2.3. Permselectivity. Apparent permselectivity was measured using the static method[19] where the potential difference across the membrane was measured while the film separated solutions of different salt concentrations in a membrane-separated cell. After clamping the film into the cell, 0.1 mol/L NaCl was circulated on one side of the

film, and 0.5 mol/L NaCl was circulated on the other side of the film. Overhead mechanical stirring was used to ensure that the solutions on either side of the film were well-mixed during the measurement. Double junction Ag/AgCl reference electrodes (RREF0024, Pine Instrument Company, Grove City, PA) were used to measure the potential difference across the film. The potential between the reference electrodes was tracked as a function of time until the potential stabilized at $\psi_{measured}$, and the standard deviation of the measured potential, $\psi_{measured}$, was typically on the order of 10^{-2} mV. The potential difference between the reference electrodes when both electrodes were immersed in the same 0.5 mol/L NaCl solution, ψ_{offset}, was subtracted from $\psi_{measured}$ to account for inherent differences in the reference electrodes. The quantity $\psi_{measured} - \psi_{offset}$ was normalized by the membrane potential difference of a perfectly permselective AEM, $\psi_{theoretical}$, to obtain the apparent permselectivity, α_{AP}:[19,20]

$$\alpha_{AP} = \frac{\psi_{measured} - \psi_{offset}}{\psi_{theoretical}} \tag{6}$$

The value of ψ_{offset} was obtained after measuring $\psi_{measured}$. The value of $\psi_{theoretical}$ can be calculated from the thermodynamic activities of the salt solutions. The activity coefficients for 0.1 mol/L NaCl and 0.5 mol/L NaCl were taken as 0.778[51] and 0.686,[9] respectively, and the value of $\psi_{theoretical}$ was calculated to be 38.1 mV.[19] Multiple measurements were averaged, and the uncertainty was taken as one standard deviation from the mean.

3. RESULTS AND DISCUSSION

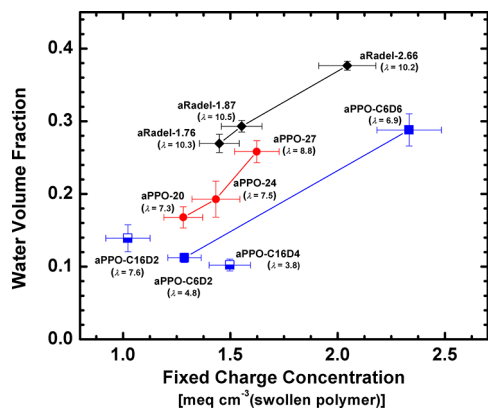**3.1. Water Uptake and Fixed Charge Concentration.** Quaternary ammonium groups on the polymer backbone increased the hydrophilicity of the material relative to the unfunctionalized polymer. The IEC of the polymer is a common measure of the degree of ionic functionalization of the material even though it does not reflect polymer swelling.[5,29] The water uptake of the aRadel and aPPO membranes equilibrated in 0.5 mol/L NaCl generally increased as the IEC of the polymer increased (Figure 2A). The water uptake of the aPPO-C16Dx samples decreased as the IEC of the samples increased, which may be due to nanophase separation and C16 alkyl chain associating in these samples.[52]

The fixed charge concentration in hydrated membranes is generally expected to increase with IEC as is shown for the samples in this study (Figure 2B). Since water uptake can increase greatly with IEC for a given polymer backbone, the fixed charge concentration of some polymers goes through a maximum when plotted versus IEC.[53] In such materials, the fixed charge concentration actually decreases with IEC above a certain degree of functionalization due to the large water uptake of the sample. The polymers considered in this study, however, do not swell so significantly as to display a maximum in fixed charge concentration versus IEC.

While water uptake is a convenient measure of water content, the volume fraction of water in the hydrated polymer, ϕ_w, is of interest from theoretical and modeling perspectives. Accurate determination of water volume fraction relies on knowledge of the density of the hydrated material, which is often difficult to determine, so water volume fraction is often determined using the dry polymer density (eq 2) and by assuming volume additivity, which has been shown to be reasonable for some charged polymers.[48] The data in Figure 3 suggest that, for a given fixed charge concentration, water volume fraction of these hydrated membranes follows trends that are similar to those relationships discussed in regard to Figure 2A. However, this correspondence between water uptake and water volume fraction may not hold for membranes with drastically different densities than those reported here, such as Nafion. Different
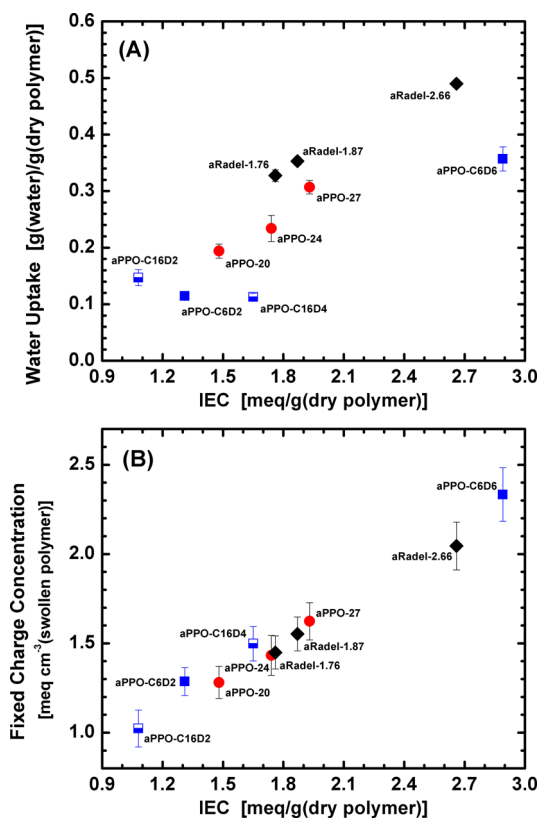
Figure 2. (A) Water uptake of AEMs (equilibrated in 0.5 mol/L NaCl) increased with the IEC of the polymer. (B) Fixed charge concentration (calculated using eq 3) increased monotonically as the IEC of the polymer was increased.

Figure 3. The volume fraction of water absorbed in the polymer increased with fixed charge concentration. The hydration numbers for each sample are listed in parentheses in units of $mol(H_2O)/eq$, and the solid lines are drawn to guide the eye.

water volume fractions can be accessed at a given fixed charge concentration by varying the composition of the polymer backbone, e.g., comparing aPPO-C16D4 and aRadel-1.76, further suggesting that the details of polymer backbone composition influence membrane swelling in water.

3.2. Ion Transport Properties. *3.2.1. Ionic Resistance.* The ionic resistance of the polymers considered in this study is reported as the intrinsic or specific ionic resistance, i.e., resistivity (Ω m). This intrinsic resistance is calculated by normalizing the measured area resistance by the film thickness (eq 5). Provided that the film is homogeneous, the intrinsic

ionic resistance can be used to calculate the area resistance of a particular polymer prepared as a film of desired thickness, which is often needed to predict process performance.[18,19]

For the polymers considered in this study, ionic resistance decreased as the fixed charge concentration of the polymer increased (Figure 4). This result is consistent with other reports
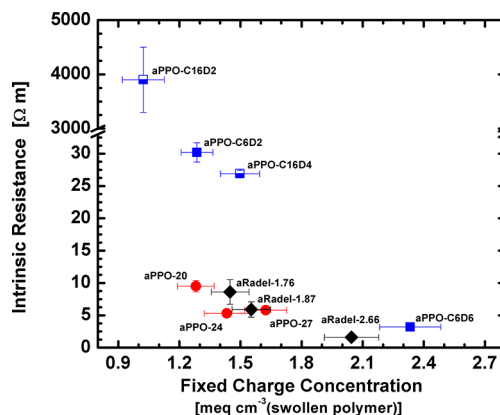
Figure 4. Intrinsic resistance decreased as the fixed charge concentration of the polymer increased.

in the literature as indicated in the Introduction. While ionic resistance correlates with fixed charge concentration, hydrophilic uncharged polymers and solutions do not have physically meaningful fixed charge concentrations. As such, it is useful to correlate ionic resistance with the volume fraction of water in the polymer as shown in Figure 5. Such correlations are often useful for rationalizing transport through swollen polymers.[7,37,54−57]
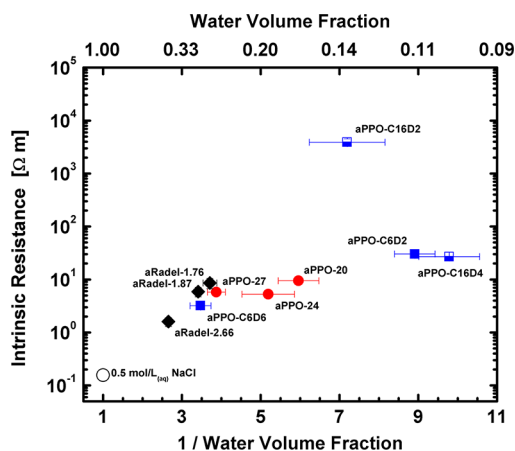
Figure 5. Intrinsic resistance of the AEMs considered in this study plotted versus the inverse water volume fraction of those polymers (equilibrated in 0.5 mol/L NaCl). The symbol (◯) at a horizontal axis value of 1 corresponds to the resistance calculated based on the conductivity of 0.5 mol/L NaCl (63.99 mS/cm).[49]

The ionic resistance of the polymers considered in this study can be varied by more than 3 orders of magnitude while the volume fraction of water sorbed in the polymer varies by a factor of 3.8 from 0.1 to 0.38 (Figure 5). Polymer ionic resistance is highly sensitive to water content, which is, in turn, linked to the fixed charge concentration of the polymer. The chemical details of the polymer (i.e., nature of the backbone, fixed charge group, etc.) can then be used to fine-tune the ionic

resistance of the polymer and/or access other beneficial properties such as chemical or thermal stability once the water uptake of the polymer has been established.

The significantly higher ionic resistance of aPPO-C16D2 compared to the other polymers may be related to the nanophase separated nature of that material.[52] Disruptions in the hydrophilic nanodomains of the aPPO-C16D2 polymer could increase the ionic resistance of the polymer because ion transport is expected to primarily occur in the hydrophilic nanodomains. The aPPO-C16D4 polymer is also nanophase separated.[52] The hydrophilic nanodomains may be better connected in aPPO-C16D4 compared to aPPO-C16D2 because the degree of functionalization in aPPO-C16D4 is double that in aPPO-C16D2, and hydrophilic domain connectivity has been shown to increase with degree of functionalization in charged polymers.[58]

The use of water volume fraction in Figure 5 allows for comparison of polymer ionic resistance and the limiting case of salt solution ionic resistance (i.e., inverse solution conductivity). The open circle in Figure 5 represents the theoretical minimum resistance that could be achieved at the salt concentration of interest (0.5 mol/L NaCl), which corresponds to a volume fraction of water of approximately 1. The position of the open circle on the vertical axis of Figure 5 was calculated from the conductivity of 0.5 mol/L NaCl, which was taken to be 63.99 mS cm^{-1} or 1.56×10^{-1} Ω m.[49] The difference between this data point and the most highly swollen polymer considered in this study gives some indication of the extent to which the presence of the polymer acts to impede ionic conduction.

3.2.1. Permselectivity. While increases in permselectivity with increasing fixed charge concentration are observed for subsets of these polymers, permselectivity generally decreased with increasing fixed charge concentration for this collection of samples (Figure 6A). This result opposes the common design guideline that high fixed charge concentration is needed to prepare high permselectivity polymers as discussed in the Introduction and suggests that physical factors beyond fixed charge concentration, such as local-scale heterogeneity, may significantly influence permselectivity.

As discussed previously, the volume fraction of water in the polymers considered in this study increased as fixed charge concentration increased (Figure 3). Permselectivity is presented as a function of water volume fraction in Figure 6B, and permselectivity generally decreased as the volume fraction of water in the polymer increased. This result suggests that increased water sorption may play a significant role in determining the permselectivity of a polymer.

In sulfonated polymers, the effectiveness of Donnan exclusion was observed to decrease as the volume fraction of water in the polymers increased, even though the fixed charge concentration, which to some extent accounts for polymer swelling, increased.[33] This result suggests that spatial variation of the electric potential within the polymer matrix may become more significant as water content increases, and this heterogeneity may become more significant than fixed charge concentration, at least in some cases.[33] The data shown in Figure 6B are consistent with this physical interpretation of Donnan exclusion and its expected effect on permselectivity. The results suggest that swelling control may be more important for increasing permselectivity than fixed charge concentration alone.
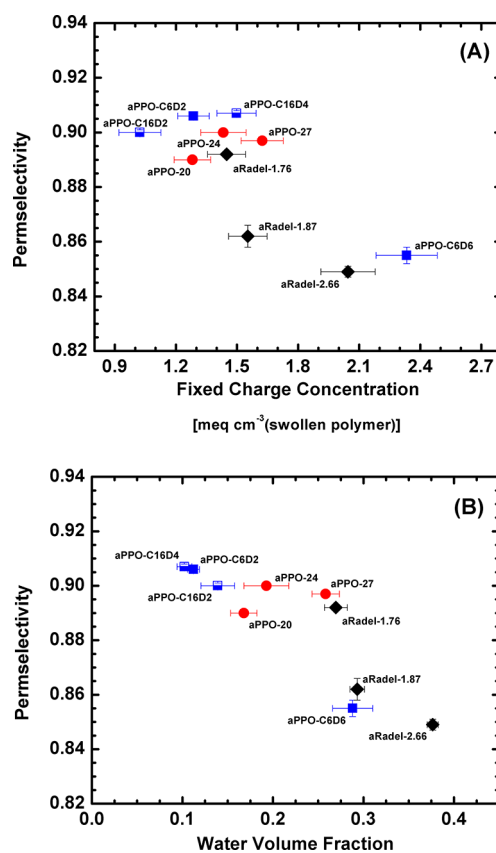

Figure 6. (A) The intrinsic resistance of the polymers decreases as fixed charge concentration increases. (B) As the polymer swells, transport of co-ions increases as well, and the increase in the volume fraction of water in the polymer (in 0.5 mol/L NaCl) drives a decrease in permselectivity even though the concentration of fixed charge groups in the polymers increases as water sorption increases (Figure 3).

3.3. The Resistance–Permselectivity Tradeoff. The previous section demonstrated the dependence of ionic resistance and permselectivity on water content. As these two transport properties that are critical for the operation of many potential-field driven processes are linked via water content, it is reasonable to suggest the existence of a tradeoff relationship between the ionic resistance and permselectivity in water-swollen membranes. Indeed, for the polymers considered in this study, two commercially available ion exchange membranes (Selemion AMV and Membranes International, Inc. AMI-7001), and data[20] from the literature, evidence of a tradeoff relationship between permselectivity and inverse intrinsic resistance (i.e., ionic conductivity) is observed as shown in Figure 7. Polymers that tend to have low resistance also tend to have low permselectivity and vice versa.

This tradeoff relationship between a measure of separation effectiveness and the mass transfer properties of a material is similar to other relationships identified in membrane science. In this particular tradeoff, polymer water content can be used to rationalize the tradeoff. As water sorption increases, the ionic resistance of the polymer decreases, but the effectiveness of Donnan exclusion is reduced by increased water sorption resulting in lower permselectivity.
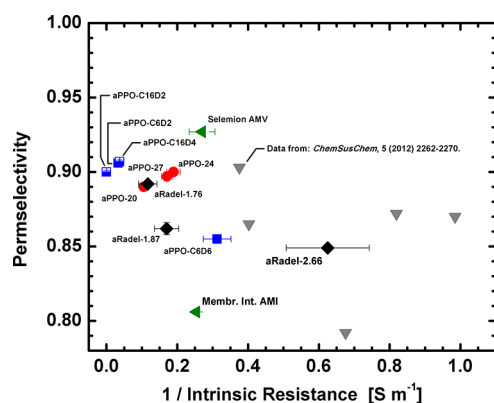
Figure 7. A tradeoff relationship exists between permselectivity and ionic resistance, and this relationship can be rationalized by the dependence of these properties on water content. Polymers with high permselectivity tend to have high ionic resistance (i.e., low ionic conductivity) and vice versa.

4. CONCLUSIONS

The ionic resistance and permselectivity of a series of quaternary ammonium-functionalized poly(phenylene oxide) and poly(sulfone) polymers were characterized in aqueous NaCl solutions, and these properties were found to be sensitive to the water content of the polymer. The intrinsic ionic resistance of the polymers was varied by more than 3 orders of magnitude by adjusting the water content and nanophase separation of the polymers, and some difference between polymer backbone types was observed. Permselectivity was sensitive to both the fixed charge concentration and water content of the polymers, and permselectivity generally decreased as the water volume fraction of the polymers increased. The use of water volume fraction for correlating and interpreting ion transport data was discussed, and water content can be used to rationalize an observed tradeoff relationship between ionic resistance and permselectivity where polymers that absorb more water tend to have lower permselectivity and lower ionic resistance and vice versa. These structure−property relationships are expected to be useful in the design and further optimization of anion exchange membranes for salinity gradient technologies.

■ AUTHOR INFORMATION

Corresponding Author
*Address: 310 Steidle Bldg., University Park, PA 16802, USA.
E-mail: hickner@matse.psu.edu.

Notes
The authors declare no competing financial interest.

■ ABBREVIATIONS

AEM, anion exchange membrane
CEM, cation exchange membrane
DF, degree of functionalization
IEC, ion exchange capacity

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