



Salt concentration dependence of ionic conductivity in ion exchange membranes



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ABSTRACT

Electric field driven ion transport in ion exchange membranes, often quantified by membrane resistance or ionic conductivity, is important for membrane-based technologies such as electrodialysis, batteries, fuel cells, etc. Various methods for measuring membrane ionic conductivity have been reported in the literature, but no widely accepted, standard protocol exists. Consequently, conflicting ionic conductivity results for widely studied commercial ion exchange membranes have been reported, leading to confusion regarding, for example, the salt concentration dependence of membrane ionic conductivity, especially for membranes equilibrated with dilute aqueous salt solutions. In this study, we report a simple, fast, reliable technique for measuring ionic conductivity based on direct contact between the membrane and electrodes. The technique was used to measure ionic conductivity values for a series of commercial ion exchange membranes as a function of external solution NaCl concentration (ranging from 0.001 to 5 M). The salt concentration dependence of membrane ionic conductivity was rationalized within the Nernst-Einstein framework. At low external solution salt concentrations (< 0.3 M), ionic conductivity values were essentially constant since mobile ion concentrations in the membranes approached a constant value (i.e., the fixed charge group concentration). At high salt concentrations (> 0.3 M), ionic conductivity values increased with increasing salt concentration for three of the membranes, presumably due to increased ion sorption owing to weaker Donnan exclusion, and decreased for one membrane, presumably due to decreased ion diffusion coefficients resulting from osmotic deswelling.

1. Introduction and background

Rapidly increasing demands for clean water and energy have led to considerable interest in membrane-based technologies for water purification and energy applications owing to their efficiency, simplicity, and small footprint [1–11]. Polymer membranes regulate small solute (e.g., water and ion) transport in such technologies due to their ability to discriminate between molecules having similar size [12]. The overall cost and efficiency of membrane-based technologies are directly related to membrane performance. The optimum membrane water and ion transport properties are dependent on the application. For example, reverse osmosis, forward osmosis, and pressure-retarded osmosis membranes must permeate water but reject ions [1]. In contrast, membranes used in electrodialysis and reverse electrodialysis must selectively permeate ions and minimize water transport [1]. Thus, fundamental design strategies for controlling water and ion transport rates in membranes are needed to improve the performance of membrane-based technologies.

Ion exchange membranes (IEMs) allow fast and selective transport of charged species (e.g., ions) [13]. This property is necessary for applications in which ion transport is driven by an electric field (e.g., electrodialysis, membrane-assisted capacitive deionization, and fuel cells, among others) [10,13]. Additionally, IEMs have attracted interest for use in technologies such as reverse osmosis and forward osmosis due to their chemical stability and ability to suppress co-ion transport (i.e., ions with similar charge to that of the fixed charges in the IEMs) [14–17].

IEMs are fabricated from polymers having ionizable functional groups covalently bound to the polymer backbone [13]. These functional groups dissociate into ions attached to the polymer backbone (i.e., fixed charges) and mobile counter-ions when contacted by water. The fixed charge groups significantly influence ion sorption and transport in IEMs. For example, highly charged IEMs in contact with aqueous salt solutions take up significantly more counter-ions than co-ions due to Donnan exclusion [13,18,19]. This characteristic is critical

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for realizing fast and selective counter-ion transport through such materials since ion transport depends, in part, on the ion concentration in a membrane [13,20]. Ion diffusion in IEMs could also be influenced by electrostatic interactions between the mobile ions and fixed charges [13,21,22].

This study focuses on electric field driven ion transport in IEMs, which is typically quantified by membrane resistance or membrane ionic conductivity [10,13]. In this study, the two terms will be used interchangeably since membrane resistivity and ionic conductivity are reciprocals of each other. Membrane resistance can be measured using a number of different techniques based on various electrochemical cell configurations employing either alternating, direct, or combined current (or potential) driving forces [10,13,23–25]. Most recent studies involve a cell configuration in which a membrane separates two (or more) compartments of flowing aqueous salt solutions, typically at the same salt concentration [23,25–36]. The electrochemical cell can consist of a two, three, or four electrode setup [23]. In this configuration, the ohmic resistance of the electrochemical cell is measured with and without a membrane, and the membrane resistance is calculated as the difference between these two values. For brevity, this type of configuration will be referred to as the “difference method”. However, many early studies employed a configuration in which the membrane was in direct contact with the electrodes during the measurements (i.e., with no flowing aqueous solution between the membrane and electrodes) [13,24,37–44]. For brevity, this type of configuration will be referred to as the “direct contact method”. A four electrode setup is considered to be advantageous over a two electrode setup since electrode reactions and polarization are not measured [45], but such a setup can only be used with the difference method. As discussed throughout this manuscript, ionic conductivity measurements using the difference method are quite difficult to perform at low external solution salt concentrations since the solution resistance often significantly overwhelms the membrane resistance.

Due to a lack of standard protocols for measuring membrane resistance and a variety of different methods used in the literature to perform the measurements, discrepancies between reported membrane resistance values for common commercial IEMs can often be found. For example, Pismenskaya et al. [46] reported an ionic conductivity value of approximately 2 mS/cm for a Neosepta CMX cation exchange membrane equilibrated with 1 M NaCl, while Galama et al. [23] reported an ionic conductivity of approximately 7.3 mS/cm for the same commercial membrane at similar conditions.

Additionally, there is some confusion in the literature regarding the salt concentration dependence of membrane resistance (or ionic conductivity), particularly for IEMs in contact with dilute salt solutions, hindering the development of a fundamental understanding of electric field driven ion transport in IEMs [23,26,27,29]. Several studies employing the difference method for measuring membrane resistance have reported rather high resistance values (i.e., low ionic conductivity) for membranes equilibrated with dilute salt solutions, in some cases several orders of magnitude greater than values observed at higher salt concentrations [23,25,26,29–31,35,47,48]. Such behavior could be caused by the presence of diffusion boundary layers at the membrane/solution interface, especially when using a DC driving force to measure membrane resistance [26–28,33,34,36,48]. This issue could be somewhat mitigated by using an AC driving force since, at high frequencies, the direction of ion transport would presumably change before a boundary layer at the membrane/solution interface is established. Perhaps the most common AC technique used today is electrochemical impedance spectroscopy (EIS) [27,33]. EIS is commonly used to characterize electrochemical properties of various materials (e.g., solutions, electrodes, membranes, etc.) [49]. In EIS, an alternating current (or voltage) driving force is applied to an electrochemical cell over a range of frequencies, and the magnitude and phase of the cell voltage (or current) are monitored to determine the complex impedance of the system, from which the ohmic resistance of the cell can be extracted.

Alternatively, a small alternating current can be superimposed on a direct current driving force, making it possible to investigate ion transport under practical operating conditions, since most applications use a DC driving force [10,50]. EIS is useful because it allows decoupling of rate phenomena that occur on different timescales, since measurements can be performed over a broad range of frequencies. Nevertheless, unusually high membrane resistance values at low external solution salt concentrations have also been observed by some investigators using EIS [23,29]. Interestingly, to the best of our knowledge, such behavior is essentially absent in studies employing the direct contact method to measure membrane resistance [13,24,37,38,40,48,51].

In this study, we propose a simple and reliable membrane resistance measurement technique using EIS based on the direct contact method. The technique was used to measure membrane ionic conductivity values for a series of commercial IEMs over a broad range of external salt concentrations (0.001–5 M). The membrane ionic conductivity results were compared with those obtained using the difference method and with literature values. The concentration dependence of membrane ionic conductivity was interpreted within the Nernst-Einstein framework.

2. Experimental section

2.1. Materials

Two cation exchange membranes, CR61-CMP (GE Power and Water, USA) and Neosepta CMX (Astom Corporation, Japan), and two anion exchange membranes, AR103-QDP (GE Power and Water, USA) and Neosepta AMX (Astom Corporation, Japan), were used in this study. The membranes were kindly provided by the manufacturers. The CEMs and AEMs were initially in the Na⁺ and Cl⁻ counter-ion forms, respectively. The chemical structures of the membranes are based on functionalized poly(styrene-divinylbenzene), where the fixed charged groups in CR61 and CMX are sulfonate ions, and those in AR103 and AMX are quaternary ammonium ions [18,52]. Relevant membrane properties (thickness of water-swollen membranes, IEC, water content, and fixed charge group concentration) are recorded in Table 1. Prior to all measurements, membranes were equilibrated in ultrapure deionized (DI) water (having an electrical resistivity of at least 18.2 MΩ-cm and less than 5.4 ppb TOC) generated by a Millipore RiOS and A10 water purification system (Billerica, MA).

The membranes have a composite structure in which the ion exchange polymer is impregnated into a porous, hydrophobic support material to increase the mechanical properties of the membranes. The ion exchange polymer phase is continuous and considered to be reasonably homogeneous. Presumably, the fabric support does not sorb

Table 1
Properties of the membranes used in this study.

Membrane	Reported IEC [meq/g (dry polymer)] ^a	Hydrated thickness (cm)	$C_A^{m,w}$ [mol fixed charge groups/L (water sorbed)] ^b	Pure water uptake, w_u , [g (water)/g (dry polymer)] ^a
CR61	2.2 (min)	0.06	3.21 ± 0.08	0.84 ± 0.01
AR103	2.2 (min)	0.06	3.58 ± 0.07	0.65 ± 0.01
CMX	1.64	0.017	7.62	0.215
AMX	1.30	0.014	7.93	0.164

^a IEC, hydrated thickness, and pure water uptake values were taken from the literature [18,27].

^b $C_A^{m,w}$ values for CR61 and AR103 were calculated from experimental ion sorption results, and $C_A^{m,w}$ values for CMX and AMX were calculated from pure water uptake and IEC values via $C_A^{m,w} = IEC \cdot \rho_w / w_u$, where ρ_w is the density of water (1 g/mL) and w_u is membrane water uptake [53].

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