

Forbidden ion transport through cation exchange membranes

Chandan K. Chaudhary, Purnendu K. Dasgupta^{*}

Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX, 76019-0065, USA

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ABSTRACT

Cation exchange membranes (CEMs) are widely used in many applications. The fixed anionic groups e.g., COO^- , $-\text{SO}_3^-$, etc. in the polymer matrix ideally allows the passage only of oppositely charged cations, driven by a potential or a concentration gradient. Anions, charged negative, the same as the membrane matrix, cannot pass through the membrane due to electrostatic repulsion. Such “Donnan-forbidden” passage can, however, occur to some degree, if the electrical or concentration gradient is high enough to overcome the “Donnan barrier”. Except for salt uptake/transport in concentrated salt solutions, the factors that govern such Forbidden Ion Transport (FIT) have rarely been studied. In most applications of transmembrane ion transport, whether electrically driven as in electrodialysis, or concentration-driven, it is the transport of the counterion to the fixed charged groups, such as that of the proton through a CEM, that is usually of interest. Nevertheless, CEMs are also of interest in analytical chemistry, specifically in suppressed ion chromatography. As used in membrane suppressors, both transport of permitted ions and rejection of forbidden ions are important. If the latter is indeed governed by electrostatic factors, other things being equal, the primary governing factor should be the charge density of the membrane, tantamount to its ion exchange capacity (IEC). In fabricating microscale suppressors, we found useful to synthesize a new ion exchange polymer that can be easily molded to make tubular microconduits. Despite a high IEC of this material, FIT was also found to be surprisingly high. We measured several relevant properties for thirteen commercial and four custom-made membranes to discover that while FIT is indeed linearly related to $1/\text{IEC}$ for a significant number of these membranes, for very high water-content membranes, FIT may be overwhelmingly governed by the water content of the membrane. In addition, FIT through all CEMs differ greatly among strong acids, they may still be transported as the molecular acids and the extent is in the same order as the expected activity of the molecular acid in the CEM. These results are discussed with the perspective that even for strong acids, the transport does take place as un-ionized molecular acids.

1. Introduction

Ion Exchange Membranes (IEMs) bear stationary charged groups. Although some inorganic IEMs have been demonstrated, commercial IEMs consist of organic polymer matrices in which ion-exchange sites are distributed throughout. Cation exchange membranes (CEMs) have fixed negatively charged groups such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{PO}_3\text{H}^-$, etc. while anion exchange membranes may rely on positively charged groups such as $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{SR}_2^+$, etc. With each type of membrane, an oppositely charged ion can pass through while a similarly charged ion does not enter the membrane due to coulombic repulsion [1, 2]. IEMs are electrically conductive. Electrical charge can be carried through such membranes in the form of counterions. CEMs are extensively used in fuel cells as polymer electrolytes [3,4] and in manifold electrochemical technologies [5] including chlor-alkali cells [6], other

electrodialytic applications [7], redox flow batteries [8], water electrolysis [9], etc. In many applications, the system can be configured with either CEMs or anion exchange membranes (AEMs). Although some specific cases involving AEMs can be attractive [10], by far most applications utilize CEMs. Especially CEMs in the $-\text{SO}_3\text{H}$ form benefit from the high electrical mobility of the hydrated proton that endows high electrical conductivity. High electrical conductivity is essential for energy efficiency; Joule heating, as well as resulting thermal degradation of the membrane, are minimized. Further, many applications involve a highly challenging chemical environment; elevated temperatures may be involved as well. CEMs in the $-\text{SO}_3\text{H}$ form are far more chemically and thermally stable than $-\text{NR}_3\text{OH}$ form AEMs. Matrix stability can still be a problem. Major industrial applications of IEMs did not begin until fluorocarbon skeleton CEMs were devised by Grot at duPont in late '60s [11,12] and commercialized under the trade name Nafion®. Nafion

^{*} Corresponding author.

E-mail address: dasgupta@uta.edu (P.K. Dasgupta).

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IEMs have since become the benchmark CEMs for their high specific conductance and excellent chemical/thermal stability. Nafion belongs to the general class of perfluorosulfonic acid (PFSA) membranes, of which now there are several commercial variants.

Our interest lies in applications of IEMs in analytical chemistry; a recent review covers the extensive analytical applications of IEMs [13]. Our laboratory is interested in the use of IEMs as “suppressors” in suppressed conductometric Ion Chromatography (IC) pioneered by Small et al. [14]. This mode of ion separation and detection is presently the benchmark in anion analysis. Briefly, the current practice involves the separation of analyte anions on a packed anion exchange column. The effluent then passes through a H^+ -form CEM device, called the *suppressor*. As a typical eluent may be a strong base in hydroxide form, e.g., KOH, passage through the suppressor results in exchange of the K^+ for H^+ , and a background of water. At the same time, strong acid anions like Cl^- , Br^- , NO_3^- , etc. exit the device in the form of the corresponding fully ionized acids HCl, HBr, HNO_3 , etc. The device thus suppresses the background conductivity of the eluent (hence the moniker) while simultaneously boosting the conductance arising from the analyte ion, now a strong acid, permitting highly sensitive detection. A common general practice in liquid chromatography is to increase the eluting power (elution strength) during the run, referred to as gradient elution. In the present case, this can be accomplished by increasing the KOH eluent concentration during the run. One great benefit of “suppression” is that regardless of changes in the hydroxide eluent concentration (and thence conductivity), the suppressor effluent remains just water, resulting in a constant low conductivity background. It will be obvious, however, that the originally H^+ -form CEM will eventually be converted to the K^+ -form, thus ceasing to function. As a countermeasure, the membrane is continuously regenerated; while eluent KOH flows on one side, a strong acid flows on the other side to maintain the cation exchange sites in the H^+ -form. If mass transfer to the membrane is not the limiting process, the proton gradient across the membrane will drive the exchange process to quantitative conversion [15]. The necessary protons can also be supplied by electrolysis of water [16]; however, chemical regeneration by a strong acid offers the simplest arrangement and is often considered the benchmark for low noise suppressor performance [17].

The current practice of IC centers on the conventional scale with column i.d.'s in the 2–4 mm range, with appropriately scaled suppressors [18]. Like all other areas, efforts to miniaturize continue; attractive IC performance has been demonstrated with column i.d.'s as small as 20–25 μm [19, 20, 44]. That suppressor fabrication in this scale is challenging is an understatement. Although electrodialytic suppressors, of $\sim 40 \mu m$ hydraulic diameters were demonstrated [21], simpler tubular chemical suppressors of an even smaller bore would be desirable. One approach is to cast a moldable ion exchange polymer/prepolymer around a tungsten wire mandrel, cure/complete the polymerization and remove the wire after solvent swelling the cured polymer. Because such a moldable ion exchange material was not readily available, we made a series of polymers based on varying ratios of poly(vinyl alcohol) to styrenesulfonate. Some of these IEMs exhibited very high IEC (exceeding that of Nafion) and water absorption. Microchannels were successfully made with this polymer in the intended fashion using tungsten wire mandrels [22]; an example is shown in Fig. S1 in the supplementary information. Later, successful chemically regenerated suppressor performance and chromatographic utility were also demonstrated [23].

An important performance determinant of a chemically regenerated CEM suppressor is zero to very limited forbidden ion transport (FIT), i.e., that of the anion of the regenerant acid. Although in principle transport of an ion of the same sign as the membrane matrix is forbidden, when the concentration differential is high enough, the Donnan barrier is overcome and the regenerant acid in molecular form can be transported across the IEM. This is much lower than the transport rate of a permitted ion, and in many applications, may be negligible overall; under

comparable conditions without an applied electric field, permitted ion transport occurs at rates far greater than FIT [24]. An electric field that promotes the membrane counterion transport would further increase this difference. However, FIT greatly affects chemically regenerated suppressed IC as the detector background will no longer be just pure water.

If electrostatic repulsion is the primary determinant of how well FIT is prevented, *prima facie* one would conclude that FIT will be inhibited by increasing functional group density in the IEM, more commonly expressed in terms of its ion exchange capacity (IEC, meq/g) or the equivalent weight (EW, 1000/IEC). Although the polystyrene – poly(vinyl alcohol) polymer used for molded suppressor fabrication had a high IEC [22], the FIT through this membrane was surprisingly high. A low suppressed conductance background was only possible with a polymeric acid regenerant where the large size of the multiply charged polymer anion minimized FIT [23].

Only one study, now dated, has investigated FIT for a few IEMs [24]. Based on theory, they proposed that FIT should be a quadratic function of the forbidden ion concentration; and verified this for several different counterions for one membrane (Nafion, EW 1100). There was no attempt to decipher how different IEM properties may relate to each other or to FIT.

In the present study, we have measured ion exchange capacities and water absorption of 13 different commercially available CEMs, and three custom synthesized CEMs that variously have fluorocarbon or hydrocarbon skeletons or are based on poly(tetrafluoroethylene) (PTFE) sheets in which an aromatic monomer is radiation grafted and then sulfonated. Using dilute perchloric acid as a model regenerant, we also measured the transport of this forbidden ion through these CEMs at multiple concentrations. Finally, these data are analyzed for insights as to how these parameters may relate to each other.

2. Experimental

2.1. Materials

Ion exchange membranes (Fumasep, Fumapem, and Nafion membranes were purchased from <http://www.fuelcellstore.com>. Aquivion membranes were a gift from the manufacturer. The radiation-grafted PTFE membranes, used in commercial membrane suppressors, were a gift from Thermo Fisher Scientific. These are prepared by soaking thin PTFE sheets in a solution of vinyl benzyl chloride and radiation grafting the latter into the PTFE matrix by γ -radiation exposure in a ^{60}Co pit. Sulfonation of the grafted aromatic moiety is then conducted with concentrated H_2SO_4 . A polyvinyl alcohol (PVA)-styrenesulfonate membrane was made as described in [22]. High density polyethylene (HDPE) capillaries, $20 \pm 1 \mu m$ in i.d. and nominally 365 μm in o.d. were custom extruded by <http://www.zena-membranes.cz> [25]. These capillaries were sulfonated by 10 % chlorosulfonic acid in dichloroethane for 30 min at 55, 65, 70, and 80 °C then allowed to remain in the same solution for 24 h at room temperature. (CAUTION: Chlorosulfonic acid is extremely corrosive and reactive. It hydrolyzes explosively in contact with water. Use minimum amounts at a time in a well-ventilated hood). The capillaries are washed subsequently with dichloroethane to remove residual $ClSO_3H$. The sulfonyl chloride functionalities formed were hydrolyzed to sulfonate by soaking in 1 M NaOH at 95 °C for 1 h. This was followed by soaking in 10 mM H_2SO_4 overnight and flowing the same through the lumen to convert to the H^+ form.

2.2. Equipment

A model 19 Thelco vacuum oven (Precision Scientific) was used for drying the membranes prior to water sorption measurements. A CDM-I conductivity detector (www.thermofisher.com), calibrated with 1 mM KCl, was used for all conductivity measurements. For the measurements with the HDPE CEM capillary, a special low-volume tubular capillary

conductivity cell [23] was used; this was independently calibrated.

2.3. Pretreatments

All as-received membranes were first cut into rectangular/square pieces with dimensions ranging from 2 cm × 2 cm–5 cm × 5 cm. Membranes were then washed thoroughly in deionized (DI) water. To *activate*, the membranes were first boiled in 10 % HNO₃ for 30 min; this or similar treatments are recommended by most manufacturers prior to use. As the membranes already come in sulfonic acid form, it is not abundantly clear the nature of the change(s) the membranes undergo by such treatment. However, we do observe that except for IEC, all the other parameters change upon such treatment. Unless explicitly so stated, all reported data pertain to such *activated* membranes. For IEC and water sorption measurements, the membranes were vacuum dried overnight at 75 °C and –660 mm Hg pressure.

2.4. Water sorption measurements

Water sorption was measured for both as-received (then thoroughly washed in DI water) and *activated* membranes. The CEM aliquot was vacuum dried as above, allowed to cool in a closed container and then weighed as rapidly as possible to minimize moisture uptake. It was then placed in DI water for 2–3 h. After withdrawal, any residual superficial liquid water was blotted off with non-shedding absorbent paper and the wet weight was measured; the balance enclosure contained a wet sponge to maintain saturation RH.

2.5. Ion exchange capacity measurements

Ion Exchange Capacity (IEC) was measured by alkalimetric back-titration. A pre-weighed dry H⁺-form membrane portion was cut into very small pieces to promote diffusion in and out of the matrix. The pieces were washed with DI water 3–4 times and then placed in a 50-mL beaker. A known excess of a primary standard ~0.0100 M Na₂CO₃ solution was added, the mixture containing the membrane slush was agitated for a period to achieve equilibration. After adding ~2 drops of 0.1 % phenolphthalein as an indicator, the mix was titrated with a secondary standard 0.0094 M HCl solution until the pink color was discharged. The slush was filtered to retrieve the membrane pieces, washed with 2 M H₂SO₄ and then left soaking in 2 M H₂SO₄ with agitation for ≥ 2 h. The acid was changed with a fresh portion at least 10x, allowing 2 h for equilibration each time to assure complete reconversion to the proton form. The membrane aliquot was again thoroughly washed with DI water before repeating Na₂CO₃ addition, back titration, etc. This whole process was repeated at least one more time. As a minimum, triplicate measurements were made. IEC measurements were also made for as-received membranes, but the results were indistinguishable within experimental error and are not separately discussed.

2.6. Forbidden ion transport measurement

A 25-mm acrylic filter holder was modified with miniature polypropylene tees on each side. The horizontal arm of each tee was provided with one inlet tube on each side as shown in Fig. 1. On each side, the inner inlet tube is placed close to the membrane surface so that the inlet liquid can efficiently wash the surface of the IEM affixed in the holder. The annular gap at the tee terminus is blocked with hot-melt adhesive so the liquid exits through the perpendicular arm of the tee. A test acid solution entered the donor side of the membrane @ 0.5 mL/min with the effluent sent to waste while the other side of the membrane was washed with DI water @0.5 mL/min and the effluent conductance measured by a calibrated conductivity detector. The conductance values of known concentration of the respective dilute acids were measured in the relevant domain using the same detector. Thus, the measured effluent conductance values in the FIT experiments could be translated to molar concentrations. The PVA-SS polymer used in this experiment contained 25 % styrenesulfonic acid by weight with an IEC of 1.35 meq/g.

Forbidden ion transport through Nafion 117 was measured with 4 different strong acids (HClO₄, H₂SO₄, HNO₃, and HCl) in concentrations ranging from 1.00 meq/L – 100. meq/L. For all the other CEMs, only HClO₄ was used for the FIT study in the 20.0–100.0 meq/L range. The FIT through the tubular HDPE CEM was measured using a setup like that described in [24].

3. Results and discussion

3.1. The forbidden ion flux J in mol/s for a non-porous homogeneous membrane is given by

$$J = P_{FI} * \Delta C * A / t \quad (1)$$

where P_{FI} is the permeability coefficient of the CEM for the forbidden ion in cm²/s, ΔC is the forbidden ion concentration differential between the donor side and the receiver side of the membrane in mol/cm³ (as receiver side concentration is so much lower than that of the donor side, for all practical purposes ΔC is given by the donor side concentration), A is the effective area of the membrane and t is its thickness in cm. For a tubular membrane of inner and outer diameters d_i and d_o , respectively, A/t is replaced by $2\pi L/\ln(d_o/d_i)$ [26] The flux J is measured from the forbidden ion concentration C_{eff} (mol/cm³) in the receiver effluent flowing at Q cm³/s as:

$$J = QC_{eff} \quad (2)$$

The flow rate Q was 8.33×10^{-3} cm³/s (0.5 mL/min) in all experiments conducted in this paper. Most of the results are reported in this paper in terms of the relative permeability P_r of the forbidden ion, defined as

$$P_r = Jt/A \quad (3)$$

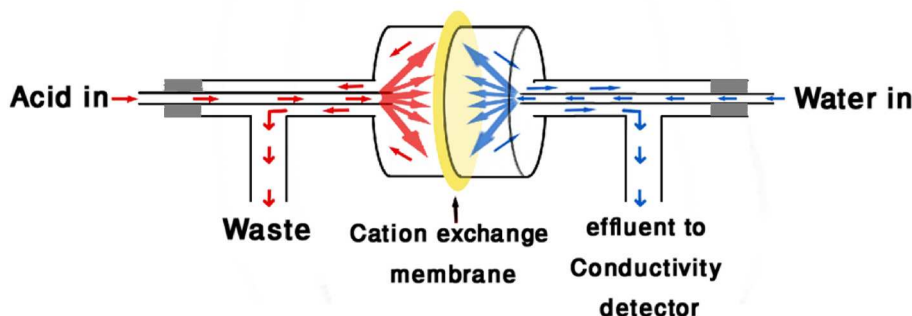


Fig. 1. Arrangement for the measurement of forbidden ion transport (FIT).

in other words, P_r is the normalized hypothetical flux that will be observed across a membrane of unit area and unit thickness under the concentration differential that is presently applied across the membrane.

3.2. Water uptake by various CEMs

Water uptake is reported here as grams of water absorbed per gram of dry polymer, both for the as-received and the *activated* membrane. Here, we report the water uptake based on triplicate measurements; uncertainties were $\leq 5\%$ relative standard deviation for all membranes studied. Many IEM parameters reported in the literature vary over a large range; the variation in reported conductivity values of the benchmark CEM Nafion is so extensive; a statistical analysis exists on 3539 records compiled from 310 original publications [27]. Water uptake is reported to be very dependent on thermal history, specifically temperature and conditions under which the membrane is dried as well as the conditions in which the membrane is equilibrated with water; this may be particularly true of Nafion 211 and 212, which are dispersion-cast membranes [28]. These membranes also show a very large dependence on water sorption if they are previously stored in water at an elevated temperature for a long period; for Nafion 212, aging decreases water sorption from $\sim 14\%$ with no aging to $\sim 8\%$ after aging at 90 % RH for a year [29]. Even for Nafion 117, the best studied CEM, Barragán et al. [30] reports a value of 17 % w/w, very close to the manufacturer's value of 16 %, while Nandan et al. [31] reports a value of 24 % for the same CEM.

Fig. 2 shows the data, including ± 1 SD error bars, for water sorption of some 15 membranes in *activated* and as-received form, and the values stated by the manufacturer, if available, and in some cases, values otherwise found in the literature, where measurement conditions or pretreatment history may have been different. The laboratory-synthesized polyvinyl alcohol – 25 % (w/w) styrenesulfonate (PVA-SS25) polymer turned out to have the highest water uptake (190 % w/w) among all the membranes investigated whereas the water uptake by the sulfonated HDPE capillary was too small to measure with any certainty;

neither is shown in this figure for clarity.

3.2.1. Water uptake: as-received vs. activated CEMs and the inexplicable dependence on thickness

What is universally true is that the as-received membranes always exhibit greater water sorption than their *activated* counterparts, anywhere between 1.2 and 5.0 $\times$ greater (av. 2.54 ± 0.12). Individual membranes also vary greatly in their water uptake whether in the as-received or *activated* form, ranging in the as-received case from $1.0 \pm 0.0\%$ for Nafion 212 to $43.6 \pm 1.4\%$ for Fumapem FS-715–RFS, and from $0.8 \pm 0.0\%$ to $17.4 \pm 0.6\%$ after activation for the same two membranes. Interestingly, there are 3 pairs of membranes in this set, which, according to the manufacturer, vary only in thickness. Consider (all values below pertain to the thickness of dry activated membranes), e.g., Nafion 211 (stated/measured: 25/25.4 μm) vs. Nafion 212 (51/50.8 μm); Aquivion E87-05 S (50/61 μm) vs. Aquivion E87-12 S (120/140 μm), and Aquivion E98-05 S (stated/measured: 50/58 μm) vs. Aquivion E98-15 S (stated/measured: 150/177 μm). The difference in water sorption by similar membranes of different thickness is statistically significant, but inexplicably, not always in the same direction. For example, in the case of Nafion 211/212, there is less sorption for the thicker membrane ($5.8 \pm 0.0\%$ vs. $1.0 \pm 0.0\%$) while the obverse is true for the Aquivion membranes: E87-05s/-12 S ($6.7 \pm 0.1\%$ vs. $26.5 \pm 1.1\%$); and E-98-05 S/-15s are respectively ($10.9 \pm 0.0\%$ vs. $18.5 \pm 0.1\%$). Although the absolute absorption is lower, similar differences persist in all three cases in the *activated* counterparts. Although the absolute values reported by the manufacturer or elsewhere in the literature may not be numerically identical to what we observe, the trend with thickness is the same as what we report, both for the Nafion and the E-98 series Aquivion membranes; the data for the other Aquivion membranes were not available. As to differences between our measured values and the manufacturer reported values, the one for Nafion 212 appears to be particularly large. Although not a whole lot of other measurements are available, our measurements for this membrane would appear to be too low. The reasons for this remain inexplicable, as all other parameters measured for the membrane (IEC, thickness, etc.) appear to correspond well with what has been reported. We do not report the water sorption of PVA-SS membranes in detail but have observed that any thermal treatment reduces water sorption; further, dry annealing at $\geq 80^\circ\text{C}$ result in discoloration, significant loss of water sorption ability and embrittlement.

3.2.2. Dimensional changes of activated membranes on wetting

Some manufacturers specify the maximum dimensional increase, particularly the two planar dimensions (that for thickness is less commonly specified) upon water uptake. Aquivion membranes, originally extruded and then sold in roll form, typically specify two different maximum values, one in the machine direction (MD, the direction in which the membrane is rolled, i.e., perpendicular to the long axis of the cylindrical membrane roll) and the other in the transverse direction (TD, perpendicular to MD in the plane of the membrane), generally expansion is expected to be less along MD than along TD; Aquivion E87-05 S, for example specifies $\leq 10\%$ and $\leq 25\%$ in MD and TD, respectively. MD or TD specifications are irrelevant in membranes marketed in sheet form, even if originally manufactured in a rolled form as the directions are no longer apparent. Maximum expansion in thickness is rarely specified, Nafion 117 being an exception where expansion in either planar direction or thickness is specified as $\leq 10\%$.

In any case, all the available data relate to the as-received membranes, our concern primarily centered on dimensional changes of membranes which were in use, as in suppressors, and then dried out, whether inadvertently or for other reasons. So, our interest would be on the behavior of membranes that have already been activated for use. Repeatability testing for separate pieces of activated membranes showed, however, considerable variability from one activated membrane aliquot to another in water sorption itself, such that we did not

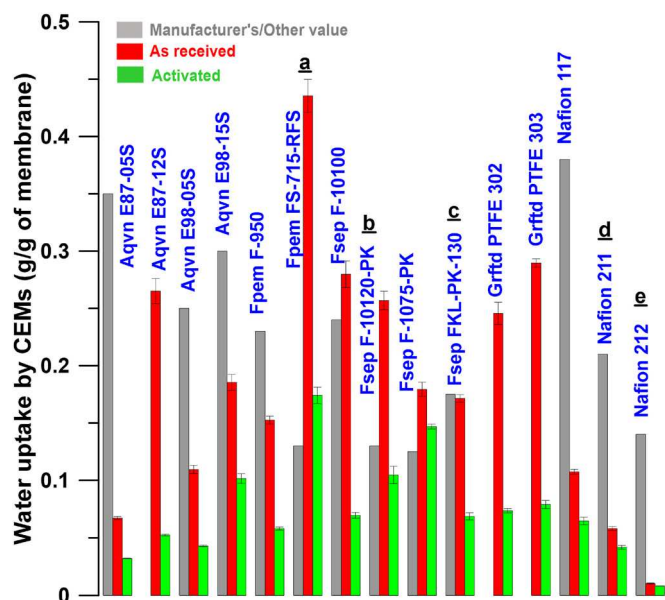


Fig. 2. Water uptake by mass. Gray: Manufacturer's or other value, Red: As received, washed and vacuum dried, Green: after boiling in 10 % nitric acid for 30 min, followed by washing with DI water and vacuum drying. The error bars show ± 1 SD ($N \geq 3$). (a–c) reference membrane dried over P_2O_5 in vacuum: (a) activated in 10 % H_2SO_4 @ 80°C , 24 h, [32]; (b) same as a but @ 100°C , 30 min [33]; (c) as received membrane stored in water for 24 h [34]; (d) ref [29]; (e) ref [35], no aging, equilibrated at 90 % RH.

feel any dimensional change measurements would have been statistically meaningful unless mean water sorption level was at least 10 % w/w, for which only a limited set of 4 membranes qualified (Aquivion E98-15 S, Fumasep F-10120-PK, Fumasep F-1075-PK, and Fumapem FS-715-RFS, water sorption ranging from 10.2 to 19.4 % by weight, increasing in the order cited), there was no relationship between dimensional changes and the degree of water sorption. None of the membranes showed a perceptible increase in thickness, and the two Fumasep membranes showed no significant changes in dimension at all. The Aquivion membrane showed the highest expansion, expanding 16 %, and 26 % in MD and TD, respectively, exceeding manufacturer's specification for the as received membranes in both cases. The Fumapem membrane expanded more modestly and comparably (5.4 and 6.7 %) in both planar directions. We conclude that the dimensional changes of activated CEMs must be determined on a case-by-case basis and cannot be estimated from the water sorption behavior.

3.3. Ion exchange capacity (IEC)

Fig. 3 shows the ion exchange capacity of various commercial membranes and the corresponding values we measured. The manufacturer's values are typically stated as the guaranteed minimum IECs. The 1:1 corresponding line indicates that indeed in all but one case (Fumapem FS-715-RFS), the measured value exceeds the stated minimum. Even for the one aberrant one (which happens to have the highest manufacturer-stated IEC), the difference is not statistically significant.

3.3.1. Water sorption and ion exchange capacity

Is there a general relationship between water sorption and cation exchange capacity of a membrane? Given that the reported water sorption values vary so much, this will be a difficult task. However, one strategy may be to consider the highest reported values because most treatments including activation or long-term hydrolytic treatment, especially at elevated temperatures [29] seem only to decrease the water sorption. For non-Nafion data, this is essentially a choice between the manufacturer reported value (if available) or the present measurements. Often there were very little difference, but we have used the higher of the values. These data are then plotted in Fig. 4 as a function of the IEC

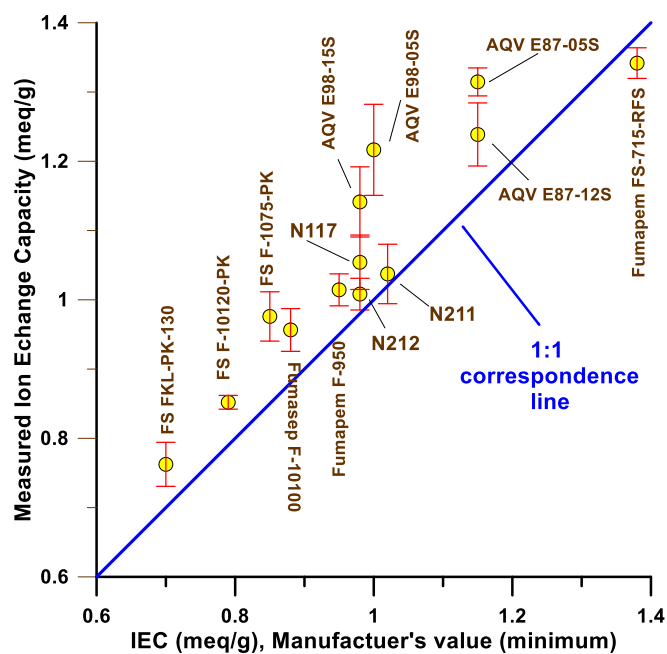


Fig. 3. Ion exchange capacity of cation exchange membranes (meq/g), measured in this work vs. manufacturer's values. The line drawn is the 1:1 correspondence line.

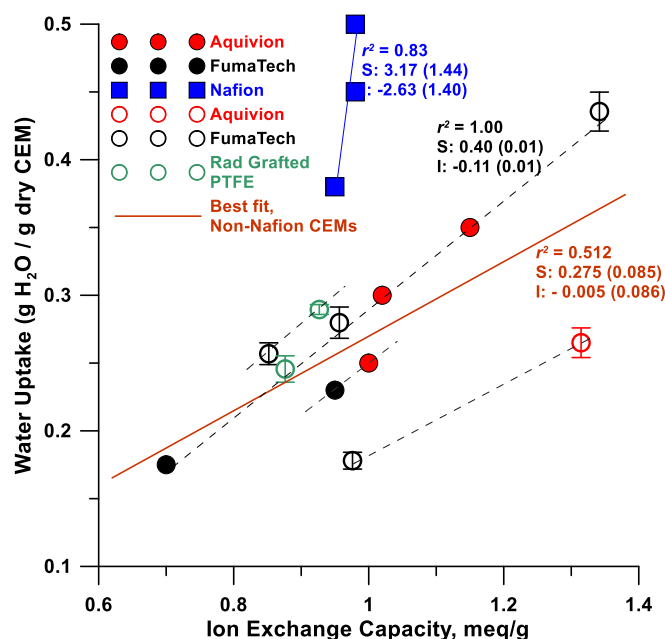


Fig. 4. Water sorption for various CEMs data as a function of IEC. Hollow symbols represent measurements made during this work and error bars represent ± 1 SD. All solid symbols represent manufacturer's data or other data in the literature. In all cases, the highest value reported for hydration conditions comparable to our experiments (room temperature equilibration in liquid water) were used. For the best fit lines, the slope (S) and Intercepts (I) are as indicated with the 95 % uncertainties in parentheses.

(again, as observed in Fig. 3, there is very little difference between ours vs. the manufacturer's data, if we have used the water sorption data measured by us, then we have accordingly used the IEC values measured by us).

It would be observed that the Nafion Membranes fall in a group by themselves. For the rest of the CEMs, the red line shows the best linear fit. Though the fit is not particularly good ($r^2 = 0.51$), the general trend of increasing water sorption with increasing IEC is clear. Of interest is that holistically these data indicate the intercept (i.e., water sorption in absence of acid groups) statistically indistinguishable from zero, and the slope to be ~ 15 water molecules per proton present (the slope indicated in the figure multiplied by 55.5, moles of water/kg). It is hard not to notice that half of the points line up very well in a single straight line, these have a small but slightly negative intercept (perhaps indicating a greater hydrophobicity of the matrix for these membranes) and a slope that corresponds to a proton hydration number of 22.3 ± 0.4 . As a benchmark, the hydration number for a fully hydrated Nafion pore is taken to be 22.5 [36]. Of the remaining six points, if sorted in three pairs paralleling the other six, two pairs exhibit slopes corresponding to hydration numbers of 22.2 and 24.2, respectively. The third, bottom-most pair, has a lower slope with a hydration number of 14, close to the data described by the dashed best-fit line.

These entire group of non-Nafion CEMs represent a significant range of IECs, as such proton hydration numbers can be calculated from the slope of a plot like that in Fig. 4.

Available Nafion CEMs do not offer the opportunity of calculating the hydration number from the slope due to the lack of significant variations in IEC, the hydration number has traditionally been calculated from the water sorption of a given membrane and its IEC. For a CEM based on a highly hydrophilic matrix, this approach cannot account for water sorption by the matrix itself. Consider the data in Fig. 5 for a series of PVA-styrenesulfonate CEMs IEC, where the PVA:styrenesulfonate ratio was varied to change the IEC [22]. The slope of the water sorption vs. IEC for this membrane indicates a hydration number of 90 ± 3 , aside from the positive intercept indicating a high hydrophilicity of the

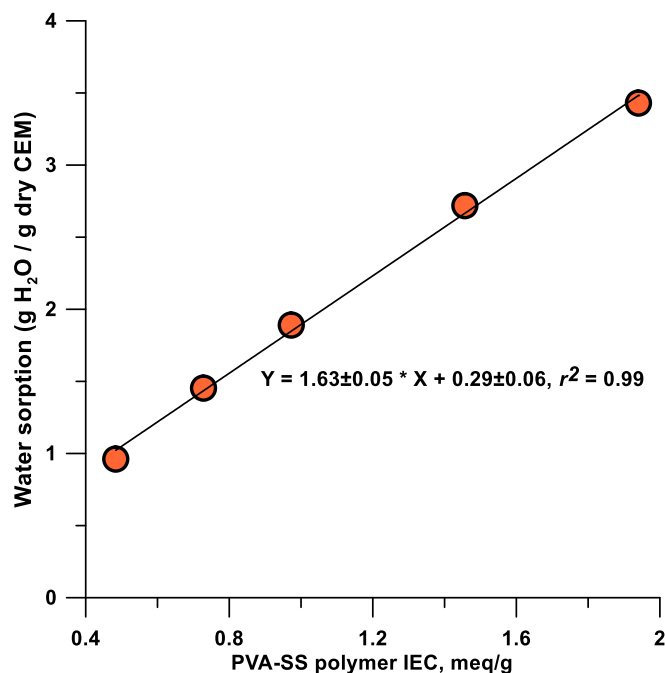


Fig. 5. Water sorption as a function of IEC, PVA-SS polymer [22].

matrix. The PVA-SS membranes can be made with even higher IECs, at the expense of their mechanical integrity. While they are not practically useful, it has previously been observed that if considerations are extended to even lower and higher IECs, water sorption is seen to be related exponentially to the IEC, the nature of the matrix itself changes with the IEC [22].

The IEC variation in Nafion polymers in Fig. 4 is too limited to conclude much from, especially when the two higher IEC CEMs (Nafion 211 and 212) are dispersion-cast and has the same IEC. Whether all three of these CEMs are considered, or the lowest IEC (Nafion 117) and any of the other two, the slope will be seen to be far higher and the intercept highly negative. With all three points here considered, *prima facie* the proton hydration number will be 175 ± 80 ; beyond the extreme hydrophobicity of the matrix, the high negative intercept suggests that if a rather low IEC Nafion type CEM were to be made, it will not hydrate in the manner those considered here do, perhaps because if homogeneously distributed, the proton site density would be inadequate for aggregation.

3.4. Forbidden ion transport (FIT)

3.4.1. Permeability of different acids through nafion 117

Transport of four common strong acids, HCl, HNO₃, HClO₄, and H₂SO₄, were measured at multiple concentrations ranging up to 0.1 M. The results are plotted in Fig. 6 in terms of permeability of the acid in moles/unit area/unit time, normalized for the membrane thickness. Sulfuric acid differs from the other acids in that it is a diprotic acid, and the second proton is ionized to an extent of ~16 % for the 0.05 M solution to ~30 % for the 0.02 M solution. So, for the most part it behaves as a monoprotic acid, and the depicted concentration reflects this assumption. As can be seen, the permeabilities vary greatly; that for HCl is so high relative to the others that this was plotted on a separate ordinate; on the other hand, that for perchlorate is very much less than any other. Fig. 7 shows the relative permeability of different membranes to three different HClO₄ concentrations.

3.4.1.1. Forbidden ion concentration in the IEM: the Helfferich model.

Helfferich [37] suggested that the molal concentration C_{FI} of the forbidden ion in the ion exchanger

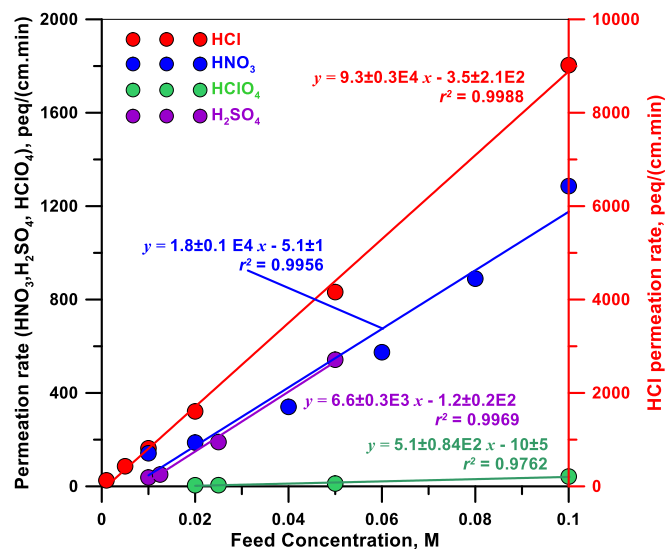


Fig. 6. Forbidden ion transport through Nafion 117 for four different acids. The coefficients of determination for the linear fits all indicate reasonable fits. To accommodate the very high permeability of HCl, the ordinate axis has a break, and no line is drawn through the HCl data. If only the higher concentration data are chosen, the fits improve significantly for HClO₄ and HNO₃. The lines shown are the best fit lines that take all data into account while the statistics shown are for the three highest concentrations. Only for HNO₃ are the fits markedly different for all data vs the three highest concentrations, with markedly different slope and intercept: those for three lowest concentration points being $y = 5.2 \pm 0.6 E2 x + 5.0 \pm 3.3$, $r^2 = 0.9878$.

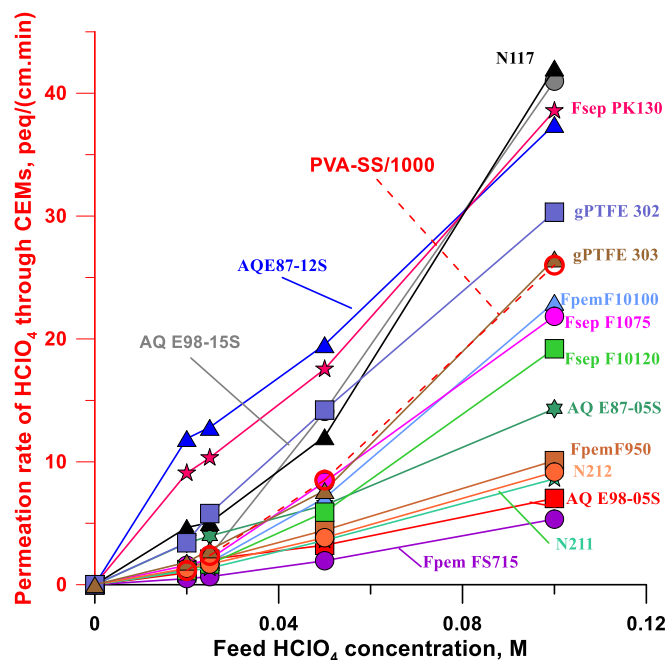


Fig. 7. Transport of HClO₄ through a large number of CEMs. Transport through the sulfonated HDPE tube was too small to measure while that through PVA-SS fit on the same graph only when the ordinate values were divided by 1000. When so divided, the PVA-SS data were practically superimposable on one of the grafted PTFE CEMs.

$$C_{FI} / m_{FI} = \sqrt{a^2 + B} - a \quad (4)$$

Where C_{FI} is the molal concentration of the forbidden ion in the resin/membrane phase (to which the FIT would be directly related to), m_{FI} is the molality of the forbidden ion that the membrane is being exposed to and a and B are respectively given as

$$a = \frac{m_R}{2z m_{FI}} \quad (5)$$

m_R being the molality of the ion exchange sites, effectively related to the IEC, z is the charge magnitude of the forbidden ion, and

$$B = \left(\frac{\gamma}{\gamma_R} \right)^2 \left(\frac{a_w}{a_{wR}} \right)^{v_{FE}/v_w} \quad (6)$$

where γ is the activity coefficient of the forbidden ion in the solution, γ_R is the activity coefficient of the forbidden ion in the exchanger phase, a_w is the activity of water in the solution, a_{wR} is the activity of water in the ion exchanger phase, v_{FE} is the partial molar volume of the electrolyte comprising forbidden ion in the solution and v_w is the partial molar volume of water.

Helfferich's equation was derived primarily on electrostatic grounds for a situation where an ion exchange membrane or resin is exposed to a concentrated electrolyte solution, as for example during most industrial ion exchange processes, including electrolysis of brine. In the present case, the IEM is exposed to relatively small electrolyte concentrations and all the parameters that constitute B is expected to be reasonably constant for a given membrane submerged in a sub-decimolar acid solution. Rearranging eqn 4 gives:

$$C_{FI} = \sqrt{\frac{m_R^2}{4z^2} + B m_{FI}^2} - \frac{m_R}{2z} \quad (7)$$

It is easy to see that as $m_{FI} \rightarrow 0$, the second term under the radical also approaches zero and so does C_{FI} ; this is intuitive as well of course: there can be no forbidden ion content in the membrane in the absence of forbidden ions. On the other hand, at high values of m_{FI} , under conditions when the first term under the radical becomes negligible relative to the second, C_{FI} would be linearly related to m_{FI} with an intercept that will be negative. It is important to note that we have no way of determining C_{FI} per se, what is plotted in Fig. 6 as the ordinate is the transport rate which we are presuming to be linearly related to related to C_{FI} modified by differences in the diffusive transport with the different acids. The statistics for the three highest concentrations all show a good linear correspondence and a negative intercept as eqn 7 at high m_{FI} ; unfortunately, any further agreement ends there.

First, at high m_{FI} , the slope would be equal to $\sqrt{B}$, this varies over two orders of magnitude from perchlorate to chloride, a degree of difference that is not possible to account for by differences in the diffusion coefficients. Second, apart from H_2SO_4 (where effective z may be somewhat higher than 1), the intercepts should all be the same (note that m_R is the same as the IEC in meq/g), not vary over orders of magnitude.

3.4.1.2. Transport of $HClO_4$ through various CEMs. We chose $HClO_4$ for further studies as it showed the least FIT among the common acids; water blank plus four $HClO_4$ concentrations from 0.02 to 0.10 M was studied (Fig. 7). Overall, the FIT values are nonlinear with concentration, particularly at lower concentrations, albeit simple linear regression, which is affected disproportionately by the higher concentration data will indicate linear r^2 values of minimally 0.98 throughout. Fig. S2 in supporting information shows the linear fits of the data including the slope and the intercept and r^2 . However, ideally a zero intercept would be expected (no FIT in the absence of the forbidden ion); in reality, in most cases the intercept was statistically non-zero; both negative and positive intercepts were indicated. We ascribe the negligible FIT through the HDPE capillary also due to its very low water sorption (see section

3.2).

Unlike the case of different acids, here we are dealing with a single permeant and an assumption that the overall transport rate will be proportional to C_{FI} , and is far more defensible than across a range of permeants. Indeed, if we assume that the observed FIT is proportional to C_{FI} and further that C_{FI} can be obtained by eqn. 7, with the individual IEC values used for m_R and arbitrary best fit B -values are obtained for each CEM, remarkably good predictions are seen (Fig. 8).

3.4.1.3. $HClO_4$ transport through different CEMs: dependence on IEC.

Although the permeabilities are not completely linear with concentration (perfect linearity will mean that the permeability constant, P_{FI} , is independent of the concentration differential) use of the best linear fit slope data (dependence of the permeation rate on concentration) provides the best single index of forbidden ion permeability across the concentration range presently studied. The slope data are given in Fig. S2 in the supporting information; presently they are plotted in Fig. 9 as a function of the different IEC values.

3.4.2. Is it really forbidden ion transport? Transport as the molecular acid?

There are few actual studies on forbidden ion content of an IEM immersed in a dilute electrolyte, what literature exists generally address the salt content of the membrane when immersed in concentrated salt solutions, e.g., the NaCl content of Nafion as a function of external NaCl concentration [38]. The Helfferich model is singularly unable to explain the differences in FIT among the different acids for the same membrane. Differences in diffusion coefficients between perchlorate and chloride is simply inadequate to explain more than a 2 orders of magnitude difference in the FIT.

When immersed in a dilute acid solution, an additional and/or alternative mode of transport may be invoked: the transport of the uncharged molecular acids. While one does not customarily think of any uncharged molecular acids when dealing with HCl, HNO_3 , H_2SO_4 , or $HClO_4$, a proton-form CEM such as Nafion 117 is an extremely acidic matrix, the proton activity has been reported e.g., to range from ~ 1.2 at 298 K [39] or equivalent to that in 1.1 M H_2SO_4 [40] and to much higher values at higher temperatures or in solvents that remove the water from the IEM [39,41]. If the transport of the forbidden ion takes place as the

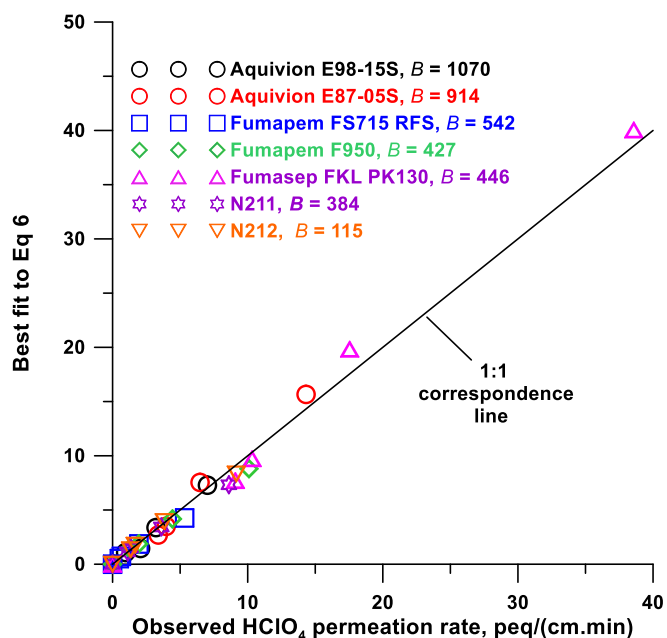


Fig. 8. The best fit (eqn 7, B -values indicated in the legends) $HClO_4$ permeabilities are plotted against the observed data. Placement on the solid line would indicate a perfect agreement.

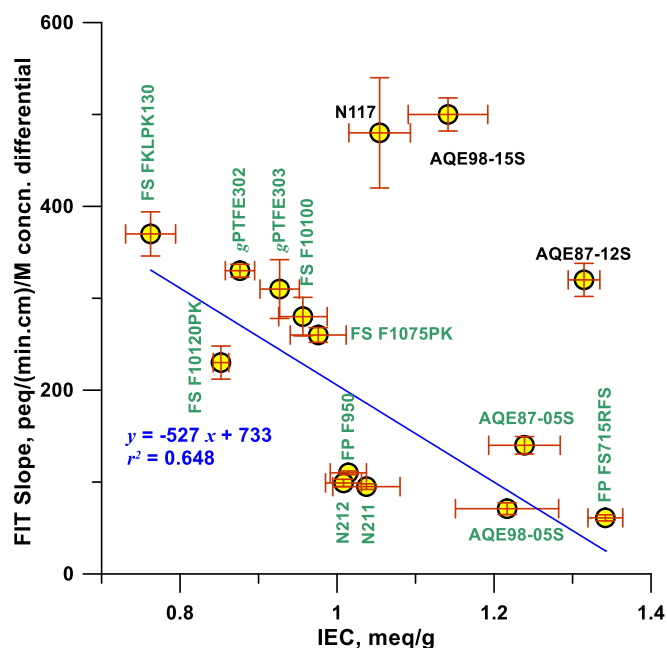


Fig. 9. The FIT vs. concentration slope (see Fig. S2 in the supporting information) plotted against the IEC. Although correspondence is admittedly far from exemplary, all but three of the CEMs (indicated by membrane names in black type face, see the web version of the paper for references to color) fall along the best-fit (that excludes the three CEMs mentioned above) line in blue, indicating a general decrease in FIT with increasing IEC, as would be expected on electrostatic grounds.

uncharged molecular acid, then the transport is not related to C_{FI} but to the activity of the corresponding unionized molecular acids present in the IEM. This activity can also be expressed in terms of the partial pressure p_i of the acid i in the CEM, p_i being given as

$$p_i = \frac{C_{FI} \alpha_0}{K_H a_w} = \frac{C_{FI} a_H}{K_H a_w (K_a + a_H)} \cong \frac{C_{FI} a_H}{K_H a_w K_a} \quad (8)$$

Where α_0 is the fraction of the undissociated acid given by $\frac{a_H}{K_a + a_H}$, a_H being the proton activity in the CEM and K_a being the dissociation constant. Dividing the concentration of the undissociated acid in the membrane by the applicable Henry's law constant K_H and the activity of the water in the membrane then gives p_i .

It is interesting that the dissociation constants of strong acids have often been measured by the dependence of the vapor pressure as a function of concentration and the Henry's law constant (K_H). The literature on HCl is particularly extensive, a more recent computational study (that also includes a review of the prior literature) suggests a pK_a of -6.23 to -6.22 [42]. The same group has also provided similarly obtained pK_a data for HClO_4 and H_2SO_4 , respectively being -10.8 and -8.6 to -4.5 [43].

In eqn 8, as a first approximation, under the same conditions, each of the parameters in $\frac{C_{FI} a_H}{a_w}$ will be the same or at least comparable, for the different acids at the same concentration. In that case, the transport will be proportional to $\frac{1}{K_H K_a}$. Because of the way in which it is measured, often the product $K_H K_a$ is what is specified, rather than individual values of K_H and K_a . The NIST lists this value for HCl to range from 1.7×10^5 to 2.0×10^6 (geometric mean, GM , 5.8×10^5) [44] and for HNO_3 to range from 3.5×10^5 to 2.4×10^6 (GM 9.2×10^5) [45]. NIST does not provide $K_H K_a$, or either value individually for HClO_4 . For H_2SO_4 it lists K_H values of 10^{11} to 5×10^{14} with the caveat that these values are order of magnitude approximations based on measurements of relatively concentrated solutions and values in more dilute solutions are likely to be higher [46]. The K_H values provided by Levanov et al. [43] for H_2SO_4

are indeed higher (0.30 – 9.2×10^{17} , GM 1.7×10^{17}), using their mean K_a value for H_2SO_4 of 3.6×10^6 , one obtains a $K_H K_a$ value of 5.9×10^{23} . Levanov et al. [43] are also the only source of K_H and K_a values for HClO_4 , the GM of their K_H values being 3.2×10^{16} , the corresponding $K_H K_a$ value is thus 1.1×10^{28} .

Given the extreme $K_H K_a$ values for H_2SO_4 and HClO_4 , detailed quantitative considerations may be unwarranted, however the $\frac{1}{K_H K_a}$ values for HCl, HNO_3 and H_2SO_4 , normalized with respect to HClO_4 , on a log scale will respectively be $22.3 : 22.1 : 4.29$. The slope ratios from Fig. 6 for the acids in the same order, again normalized with respect to HClO_4 , these are $180:35:13$. Consider also that HCl has the lowest molecular weight among the acids considered, and thus will have the largest partial molar volume that affects the B term in an exponential manner (see eqn. 6) and thus should have the largest C_{FI} . We conclude that the differences in the observed transport among different acids are far better rationalized in terms of transport as molecular acids. If this is indeed the mechanism, the term “forbidden ion” transport is inappropriate; it is uncharged molecules that are being transported.

No liquid chemical is readily available with as low an extent of contaminant ions as water. Conductivity detection technology is inexpensive and with appropriate thermostating can favorably compete with mass spectrometry to detect and quantify small amounts of impurity ions in water. Careful conductometric measurement of permeation rates of acids as a function of concentration through a CEM may provide a uniquely facile measurement method to measure both K_H and K_a for strong acids.

3.4.3. The abnormally high FIT through the PVA-SS membranes

The PVA-SS membrane containing 25 % by weight Styrene sulfonic acid exhibited a FIT some 1000-fold higher than membranes of comparable IEC; the only other parameter in which it was exceptional was its water absorption, at 1.04 ± 0.05 %, this is more than twice the highest value reported for any other CEM. For Nafion, increasing water content has been shown to increase the dielectric constant from 4 to 20 [47], the presence of large amounts of water in the PVA-SS membrane can greatly increase the dielectric constant and reduce electrostatic interactions, leading to higher C_{FI} .

Although we do not observe heterogeneity by optical microscopy, it is possible that there is segregation of PVA and styrenesulfonate and there are PVA only micro/nano channels across the membrane and transport is significantly or even primarily taking place across these.

4. Conclusions

This is the first study to examine a variety of CEMs, both commercial and custom made, including one made from poly(vinyl alcohol) and styrenesulfonate (PVA-SS), for their various physical properties, notably ion exchange capacity, and water absorption (both in activated and as received forms measured by us as well as values that have been reported, either by the manufacturer or if not available, by others) as well transport of a strong acid, normally forbidden.

First, as to IEC, our measurements validate manufacturer specifications in all cases. The water content of activated membranes, in the form of they are used, are generally not available in the literature. All commercial CEMs absorb substantially less water in activated form. As to water absorption in as-received form, our measurements do not necessarily agree with manufacturer's values, and neither set are always higher or lower compared to the other. Further, the values in the activated form, while uniformly lower, are not linearly correlated with our as-received measurements or manufacturer's values. For Nafion 117, perhaps the best-studied benchmark, it is known that thermal or hydration history greatly affects water sorption. In our experience, any pretreatment, even dry storage, including refrigerated storage, only decreases water sorption.

Water sorption by CEMs has often been denoted by hydration

number, expressed as moles of water absorbed divided by the moles of protons present. This ignores any influence the matrix may have on the hydration. All but two of the CEMs we have examined are similar in that they all have perfluorocarbon backbones, but details differ in several aspects, importantly including the IEC and the chain lengths connecting the -SO₃H group to the main structure. The significant differences in the IECs among the ensemble allows one to examine the proton hydration number as the slope of a plot of water sorption as a function of the IEC; this is in the range of 15 ± 5 with a large uncertainty in the intercept (indicating variation in the influence of the matrix on hydration). Such analysis is not possible for the Nafion® polymers, the range of IEC is too small and the observed difference in hydration is more likely due to the difference in how the membrane is made (extrusion as the sulfonyl fluoride vs dispersion-casting in the fully hydrolyzed form). The profound influence of the matrix on the “proton hydration number” is readily noted for the PVA-SS class of polymers where the IEC is systematically varied over a large range – other than the significant positive intercept indicating intrinsic hydrophilicity of the PVA matrix, the slope would translate to an astounding apparent proton hydration number of 90.

The only theoretical framework of incorporation of an electrolyte including a forbidden ion was given by Helfferich largely with concentrated salt solutions as the surrounding medium. When a dilute strong acid solution is the medium, incorporation of the electrolyte may be explicable by the Helfferich model but differences in the transport of different strong acids (which differ by orders of magnitude) cannot be accounted for by this model. We propose that even for strong acids it is actually the undissociated molecular acid that is transported.

Finally, transport of strong acids through a PVA-SS membrane was inexplicably some three orders of magnitude greater than perfluorosulfonate membranes of comparable IEC. We attribute this to the unusually high water-content of this membrane, increasing dielectric constant and possible microheterogeneity that may permit segregated PVA microchannels across the membrane.

Consent for publication

Written informed consent for publication was obtained from both authors.

CRediT authorship contribution statement

Chandan K. Chaudhary: Writing – original draft, Visualization, Investigation, Data curation. **Purnendu K. Dasgupta:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Purnendu K. Dasgupta reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2024.126581>.

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