

Supporting Information

Counterion Mobility in Ion-Exchange Membranes: Spatial Effect and Valency-Dependent Electrostatic Interaction

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THEORY

Derivation of the Equation for Electrostatic Interactions

When counterions migrate in a fixed-charge system, the electrostatic interactions between the mobile counterions and the fixed charges result in a “rough” potential gradient and exert a friction-like effect that reduces the mobility of the counterions. Manning, in 1967,¹ established a model to determine the diffusivity of ions moving in a locally inhomogeneous field induced by fixed charges. Here, we extend and modify his work, to derive an analytical expression for the effective diffusivity of counterions in charged membranes. For consistency, the derivation presented here will adopt the Gaussian-cgs unit system, which was used in the original study. The final results are converted to the International System of Units and the equations reported in the main manuscript are, thus, in SI units.

As shown by Manning, the ratio between effective diffusivity of an ion in the rough potential gradient of the fixed charge system, D_i^{EI} , and the diffusivity in a uniform electric field, D_i^{UN} , can be expressed as

$$D_i^{\text{EI}} / D_i^{\text{UN}} = 1 - \sum_p (p_x^2 / p^2) |\phi_p|^2 \quad (\text{S1})$$

where \vec{p} (p_x , the x value of the vector, p , the modulus) represents the coordinate vectors with distribution periodicity in the 3D space (discussed further in later paragraphs); ϕ_p is the solution for the \vec{p} -based Fourier transformation of the periodic function of the reduced potential. The Poisson-Boltzmann equation describing the counterions and the fixed charges gives ϕ_p :

$$\phi_p = \lambda c_{\text{fix}} z_{\text{fix}} z_{\text{ct}} (p^2 + \kappa^2)^{-1} \quad (\text{S2})$$

where Debye length, λ , is equal to $4\pi e^2 / \epsilon_r k_B T$ (e is the elementary charge, ϵ_r is dielectric constant, k_B is the Boltzman constant, and T is absolute temperature); κ is the Debye-Hückel screening parameter, and κ^2 can be expressed as $\lambda c_{\text{ct}} z_{\text{ct}}^2$. Note that, here, the Gaussian unit for the concentration of fixed charges, c_{fix} , is number per volume, rather than molar concentration used in the main manuscript. Substituting eq S2 into eq S1:

$$D_i^{\text{EI}} / D_i^{\text{UN}} = 1 - \sum_p (p_x^2 / p^2) [\lambda c_{\text{fix}} z_{\text{fix}} z_{\text{ct}} (p^2 + \kappa^2)^{-1}]^2 \quad (\text{S3})$$

As charge balance dictates $c_{\text{fix}} |z_{\text{fix}} z_{\text{ct}}| = c_{\text{ct}} z_{\text{ct}}^2$, eq S3 becomes

$$D_i^{\text{EI}} / D_i^{\text{UN}} = 1 - \sum_p (p_x^2 / p^2) [p^2 \lambda^{-1} c_{\text{fix}}^{-1} |z_{\text{fix}} z_{\text{ct}}|^{-1} + 1]^{-2} \quad (\text{S4})$$

Manning assumed that $p^2 \lambda^{-1} c_{\text{fix}}^{-1}$ is much larger than 1 for relatively dilute systems and then used the Taylor approximation, $1 - x \approx e^{-x}$, to formulate an analytic exponential function. It is worthwhile to note that the derived exponential expression bears resemblances to general form of the activation energy function. Applying the same simplifying assumption and approximation for multivalent ions to eq S4 yields

$$D_i^{\text{EI}} / D_i^{\text{UN}} = 1 - |z_{\text{fix}} z_{\text{ct}}|^2 (\lambda^2 \sum_p p_x^2 c_{\text{fix}}^2 p^{-6}) \approx \exp[-|z_{\text{fix}} z_{\text{ct}}|^2 (\lambda^2 \sum_p p_x^2 c_{\text{fix}}^2 p^{-6})] \quad (\text{S5})$$

For $|z_{\text{fix}}| = 1$, which is the case for practically all conventional ion-exchange membranes (IEMs), eq S5 is

$$D_i^{\text{EI}} / D_i^{\text{UN}} = \exp(-z_{\text{ct}}^2 A) \quad (\text{S6a})$$

$$A = \lambda^2 \sum_p p_x^2 c_{\text{fix}}^2 p^{-6} \quad (\text{S6b})$$

The $\vec{\mathbf{p}}$ vector can be expressed as, $2\pi (n_x / a_x, n_y / a_y, n_z / a_z)$, where n_x , n_y , and n_z are integers, except for (0,0,0); a_x , a_y , a_z describes the periodic volume unit containing a single fixed charge, with the volume of the unit, $V = a_x a_y a_z$. As the unit of fixed charge density is number per volume, c_{fix} is, hence, equal to V^{-1} . Considering the simple symmetric scenario of $a_x = a_y = a_z = a$, i.e., the unit is a cubic cell, $\vec{\mathbf{p}} = 2\pi (n_x / a_x, n_y / a_y, n_z / a_z)$ can be substituted into eq S6b:

$$A = (2\pi)^{-4} \lambda^2 c_{\text{fix}}^{\frac{2}{3}} \sum_{n_x, n_y, n_z} \frac{n_x^2}{n^6} \quad (\text{S7})$$

where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. The numerical value of $\sum_{n_x, n_y, n_z} \frac{n_x^2}{n^6} \approx 5.48$ and, therefore,

$$\begin{aligned} A &\approx (2\pi)^{-4} \lambda^2 c_{\text{fix}}^{\frac{2}{3}} (5.48) \\ &= \frac{5.48 e^4}{\pi^2 \epsilon_r^2 k_B^2 T^2} c_{\text{fix}}^{\frac{2}{3}} \end{aligned} \quad (\text{S8})$$

Converting Gaussian-cgs units used thus far to SI units yields the analytical expression for A (eq 3b of the main manuscript):

$$A = \frac{\theta e^4 N_A^{\frac{2}{3}}}{16\pi^4 \epsilon^2 k_B^2 T^2} c_{\text{fix}}^{\frac{2}{3}} \quad (\text{3b})$$

where $\theta = 5.48$, ϵ is absolute permittivity (product of vacuum permittivity and dielectric constant, $\epsilon_0 \epsilon_r$), $c_{\text{fix}}^{\text{m}}$ is molar concentration (SI unit) of the fixed charges in the membranes, e is the elementary charge, N_A is the Avogadro constant, k_B is the Boltzmann constant, and T is absolute temperature. We note that, to yield the function in analytical form, simplifications to transform eq S4 to S5 are needed, i.e., dilute system approximation and Taylor approximation, which can incur numerical imprecisions in the final model.

MATERIALS AND METHODS

Ion-Exchange Capacity

The ion-exchange capacity, IEC, of cation exchange membranes was characterized by the titration method. The membrane coupons were immersed in 1.0 M HCl solution with stirring for 24 h, then washed with deionized (DI) water. The residual water on the membrane surfaces was carefully removed. The coupons were then soaked in 50 mL of 1.0 M NaCl for another 24 h, for H^+ in the membrane to fully exchange with Na^+ . 25 mL of the rinsing solutions were pipetted out and titrated with 10 mM NaOH and using phenolphthalein as an indicator. The IEC is

$$\text{IEC} = \frac{2C_{\text{NaOH}} V_{\text{NaOH}}}{W_{\text{dry}}} \quad (\text{S9})$$

where C_{NaOH} and V_{NaOH} are the concentration and volume of the titrant NaOH solution, respectively, and W_{dry} is the dry weight of the membrane coupon (obtained using the procedure described in the following swelling degree measurement). The coefficient of 2 accounts for the volume ratio of the initial NaCl desorption solution (50 mL) to the titrated solution (25 mL).

The IEC of anion exchange membranes was determined by ion elution. The membrane coupons were soaked in 1.0 M NaCl solution for 24 h. The Cl^- -loaded IEMs were washed with DI water and carefully wiped with Kimwipe paper. The membrane coupons were then transferred to 50 mL of 0.50 M Na_2SO_4 rinsing solution to release the Cl^- . After 12 h, the membrane coupons were moved into another 50 mL of 0.5 M Na_2SO_4 solution. The concentrations of Cl^- in the two batches of rinsing solutions were analyzed using ion chromatography (Dionex Aquion, Thermo Fisher Scientific, Waltham, MA). The IEC was determined using

$$\text{IEC} = \frac{(C_{r1} + C_{r2})V_r}{W_{\text{dry}}} \quad (\text{S10})$$

in which C_{r1} and C_{r2} are the Cl^- concentration in the two batches of rinsing solution, V_r is the volume of the solution (50 mL), and W_{dry} is the dry weight of membrane coupon obtained by the procedure described in SD measurement.

The IEC of eq S10 is normalized by the mass of dry membrane and includes the counterion mass (Na^+ and Cl^- for CEM and AEM, respectively). Subtracting the contribution of counterion mass yields the IEC normalized by the mass of dry polymer only, $\text{IEC}_{\text{polymer}}$:

$$\text{IEC}_{\text{polymer}} = \frac{\text{IEC}}{1 - \text{IEC}(\text{MW}_{\text{ct}}/|z_{\text{ct}}|)} \quad (\text{S11})$$

where MW_{ct} is the molecular weight of the counterion and z_{ct} is the counterion valence.

Swelling Degree

The membrane coupons were soaked in 1.0 eq/L electrolyte solutions for at least 24 h. Residual solution on the membrane surfaces was carefully removed before each wet weight measurement and the membrane coupons were returned to the solution between measurements to ensure the IEMs were fully hydrated. The wet membranes were then dried in a vacuum oven at 35 °C for 24 h. The SD was calculated as

$$SD = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (\text{S12})$$

where W_{wet} and W_{dry} are the weights of hydrated and dry membranes, respectively.

Different counterions have dissimilar molecular weights and, hence, have varying contributions to W_{wet} that, in turn, affect the calculated SD. To account for this effect, the SD measured above was corrected using the principles of mass balance:

$$SD_{\text{corrected}} = SD \left[1 + IEC_{\text{polymer}} \left(\frac{MW_{\text{ct}}}{|z_{\text{ct}}|} \right) \right] \quad (\text{S13})$$

Polymer Density

A 2.0 mL glass pycnometer (Fisher Scientific, Waltham, MA) was utilized to measure the polymer density, ρ_p , of the membranes. First, the membrane samples were shredded into pieces and dried in a vacuum oven at 35 °C for 24 h. The dry membrane weights, m_1 , were measured. The pycnometer was filled with DI water and weighed (m_2). After the pycnometer was emptied, the shredded membranes were placed in the pycnometer and the receptacle was filled with DI water to the same full level again. The weight of the pycnometer with membrane and water, m_3 , was measured. The density of the polymer in the membrane, ρ_p , was calculated as

$$\rho_p = \frac{m_p}{V_p} = \frac{m_1}{(m_2 - m_0) / \rho_w - (m_3 - m_0 - m_1) / \rho_w} = \frac{m_1}{m_2 - m_3 + m_1} \rho_w \quad (\text{S14})$$

where ρ_w is the mass density of water at room temperature (0.9970 g/mL),² m_0 is the dry weight of the empty pycnometer (i.e., no water or polymer), m_p is the weight of the polymer, and V_p is the volume of the polymer.

Membrane Conductivity and Diffusivity Characterization

An electrochemical test setup based on a four-electrode cell system was used to characterize membrane conductivities in different electrolyte solutions.³ The two chambers of the cell were separated by a membrane coupon with an effective area of 3.14 cm² (circle of 2 cm diameter). The 1.0 eq/L electrolyte test solutions were recirculated through the two chambers during the tests. Membrane conductivity, σ^m , was measured using direct current chronopotentiometry with ten steps between 1–10 mA (detailed procedure can be found in our previous study)³. Membrane

conductivity, σ_i^m , for the specific counterion, i , was estimated with the total conductivity and measured transport number, $\sigma^m t_{ct}^m$. Counterion diffusivities in the IEMs were then calculated with eq 1 of the main manuscript using the measured conductivities, σ_i^m , and membrane counterion concentrations, c_i^m . For each membrane-counterion pair, the experiments were at least duplicated, with three conductivities recorded for each round of experiments.

Transport Number Characterization

To account for the possible contribution from co-ion transport to the conductivity, the transport numbers of the counterions, t_{ct}^m , were characterized and used to determine the conductivity specific to the counterion, $\sigma_i^m = \sigma^m t_{ct}^m$.^{4,5} The transport numbers of the counterions (except for phosphate) in the membranes were characterized using the apparent permselectivity measurement. The IEM permselectivity, α , can be defined in terms of transport numbers, t , by⁶

$$\alpha = \frac{t_{ct}^m - t_{ct}^s}{t_{co}^s} \quad (S15)$$

where subscripts ct and co refer to counterion and co-ion, respectively, and superscripts m and s denote membrane phase and solution phase, respectively. For a membrane separating two chambers with a single electrolyte solution of different concentrations (superscripts LC and HC signify low and high concentrations, respectively), the membrane potential, V_m , is related to t :⁴

$$V_m = -\frac{t_{ct}^m}{z_{ct}} \frac{R_g T}{F} \ln \frac{a_{ct}^{LC}}{a_{ct}^{HC}} - \frac{t_{co}^m}{z_{co}} \frac{R_g T}{F} \ln \frac{a_{co}^{LC}}{a_{co}^{HC}} \quad (S16)$$

where z is ion valency, a is ion activity, R is the gas constant, F is the Faraday constant, and T is absolute temperature. Since $t_{ct}^m + t_{co}^m = 1$ and further assuming $a_{ct}^{LC}/a_{ct}^{HC} = a_{co}^{LC}/a_{co}^{HC} = a^{LC}/a^{HC}$,⁴ eq S16 can be simplified to

$$V_m = \left(\frac{t_{ct}^m}{z_{ct}} + \frac{1-t_{ct}^m}{z_{co}} \right) \frac{R_g T}{F} \ln \frac{a^{HC}}{a^{LC}} \quad (S17)$$

where the activity, a , can be expressed as the product of molar concentration, c , and mean activity coefficient, γ_{\pm} . In this study, the Pitzer model was employed to evaluate γ_{\pm} .⁷ If the IEM is perfectly permselective, only counterions can permeate across the membrane, i.e., $t_{\text{ct}}^{\text{m}} = 1$. The theoretical potential in this ideal case is equivalent to the Nernst potential:^{4,6,8}

$$V_{\text{theoretical}} = \frac{R_g T}{z_{\text{ct}} F} \ln \frac{a^{\text{HC}}}{a^{\text{LC}}} \quad (\text{S18})$$

For a $\nu_+ : \nu_-$ electrolyte, an expression for t_{ct}^{m} can be obtained by substituting eq S18 into eq S17:

$$t_{\text{ct}}^{\text{m}} = \frac{\frac{\nu_{\text{ct}} V_{\text{m}}}{V_{\text{theoretical}}} + \nu_{\text{co}}}{\nu_{\text{ct}} + \nu_{\text{co}}} \quad (\text{S19})$$

where ν_{ct} and ν_{co} are the stoichiometric coefficients of counter- and co-ions, respectively. Details on the measurement of membrane potential, V_{m} , and the setup can be found in our previous paper.³ HC and LC concentrations of 1.0 and 0.2 eq/L, respectively, were used.

Since the phosphate solution has a comparatively high pH, at which hydroxide ions can potentially contribute a nonnegligible portion to anion transport, the transport number of phosphate was determined using a four-cell electrodialysis stack. The components of the electrodialysis stack, in sequential order, are: 20 mL 1.0 eq/L Na_2SO_4 (anode chamber), CEM Selemion CMV, 20 mL 0.10 eq/L Na_2SO_4 (collector chamber), AEM Selemion AMV (membrane to be analyzed), 20 mL 1.0 eq/L Na_3PO_4 (feed chamber), CEM Selemion CMV, and 20 mL 1.0 eq/L Na_2SO_4 (cathode chamber). The membrane area was 3.14 cm^2 (circle with a diameter of 2 cm). The current density applied was 10 mA/cm^2 (equivalent to an applied current of 31.4 mA). During ion permeation, the collection chamber was sampled at 10, 20, and 30 min. Phosphate concentrations of the samples were analyzed using ion chromatography. The transport number of phosphate, t_{ct}^{m} , was determined with

$$t_{\text{ct}}^{\text{m}} = \frac{V_{\text{chamber}} F |z_{\text{PO}_4^{3-}}|}{I} \frac{\Delta c_{\text{sample}}}{\Delta t_{\text{sample}}} \quad (\text{S20})$$

where I is current (31.4 mA), F is the Faraday constant, $z_{\text{PO}_4^{3-}}$ is the valency of phosphate, and V_{chamber} is collector chamber volume. The rate of change of phosphate concentration in the collector chamber is $\Delta c_{\text{sample}}/\Delta t_{\text{sample}}$. Because the exact aqueous chemistry within the IEM cannot be precisely determined, a portion of the phosphate species in the membrane may be protonated to monohydrogen phosphate, HPO_4^{2-} , inside the membrane and possess a valency of -2 instead of -3 . The protonation of some phosphate species can potentially lead to higher PO_4^{3-} mobility measurements, but such inaccuracies, if any, would be relatively small (especially as the results are analyzed on logarithmic scales). Therefore, the overall trends reported in the discussions on anion mobilities in AEM are still expected to hold.

Dielectric Relaxation Spectroscopy

Dielectric relaxation spectroscopy, DRS, in the microwave frequency range was utilized to characterize the dielectric permittivity properties of the IEMs in hydrated states. The measurements were carried out on a vector network analyzer (VNA, N9928A, Keysight, Santa Rosa, CA).^{9–11} Membrane strips (5.0 mm wide) were hydrated with DI water and wrapped tightly around the inner conductor of a coaxial transmission line sample holder (3.5 mm diameter, 5 cm length, 8043S5, Maury Microwave, Ontario, CA) connected to the VNA.^{9,10} The S-parameter of the membranes was measured over a frequency range of 45.0 MHz to 26.5 GHz and converted to relative complex permittivity.¹⁰ The dielectric constant, or relative permittivity, ϵ_{DRS} , of the hydrated membranes was extracted from the real portion of the relative complex permittivity.¹²

RESULTS

Polymer Density, Ion-Exchange Capacity, and Swelling Degree

Table S1. Dry polymer density, ρ_p , and ion-exchange capacity, IEC, of the membranes.

	Selemion CMV	Fumasep FKS	Ralex CMHPES	Selemion AMV
Type	CEM	CEM	CEM	AEM
Polymer density, ρ_p (g/mL)	1.43 ± 0.01	1.33 ± 0.01	1.17 ± 0.004	1.22 ± 0.01
Ion-exchange capacity, IEC _{polymer} (meq/g dry polymer)*	2.11 ± 0.02	1.64 ± 0.01	2.17 ± 0.005	1.95 ± 0.07

* The ion-exchange capacity here is normalized by the mass of polymer, excluding counterions.

Table S2. Swelling degree, SD, of the cation exchange membranes for different electrolyte solutions.

	Swelling degree, SD (g water/ g dry polymer)		
	Selemon CMV	Fumasep FKS	Ralex CMHPES
NaCl	0.293 ± 0.003	0.253 ± 0.009	0.465 ± 0.002
KCl	0.223 ± 0.008	0.178 ± 0.014	0.359 ± 0.006
MgCl ₂	0.257 ± 0.004	0.231 ± 0.005	0.424 ± 0.003
CaCl ₂	0.262 ± 0.001	0.220 ± 0.012	0.424 ± 0.006
AlCl ₃	0.218 ± 0.009	0.207 ± 0.002	0.396 ± 0.003
LaCl ₃	0.251 ± 0.006	0.226 ± 0.013	0.388 ± 0.009
DI water (Na ⁺ as counterion)	0.314 ± 0.007	0.240 ± 0.013	0.568 ± 0.013

Table S3. Swelling degree, SD, of the anion exchange membrane for different electrolyte solutions.

	Swelling degree, SD (g water/ g dry polymer)
	Selemon AMV
NaCl	0.183 ± 0.005
NaBr	0.150 ± 0.012
NaNO ₃	0.169 ± 0.012
Na ₂ CO ₃	0.293 ± 0.006
Na ₂ SO ₄	0.201 ± 0.004
Na ₃ PO ₄	0.244 ± 0.008
DI water (Cl ⁻ as counterion)	0.183 ± 0.003

Diffusivity

Table S4. Membrane diffusivity, D_i^m , of different counterions in Selemion CMV and the corresponding terms to determine D_i^m .

Selemion CMV	Counterion					
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	La ³⁺
Membrane resistivity, ρ^m ($\Omega \cdot \text{cm}$)	260 ± 64	152 ± 52	1,488 ± 617	1,351 ± 495	15,617 $\pm 1,906$	12,079 $\pm 2,810$
Conductivity measured, σ^m , $1 / \rho^m$ (S/m)	0.385	0.659	0.0672	0.0740	0.00640	0.00828
Counterion conductivity, σ_i^m , $\sigma^m t_{ct}^m$ (S/m)	0.368	0.629	0.0618	0.0682	0.00505	0.00655
Volume fraction of water, f_w , $\frac{SD / \rho_w}{SD / \rho_w + \rho_p^{-1}}$ (-)	0.295	0.242	0.268	0.273	0.238	0.264
Fixed charge density, c_{fix}^m , $\text{IEC} \cdot \rho_p (1 - f_w)$ (eq/L)	2.13	2.29	2.21	2.20	2.31	2.23
Membrane diffusivity, D_i^m , $\frac{R_g T \sigma_i^m}{F^2 z_i z_{\text{fix}} c_{\text{fix}}^m}$ ($10^{-11} \text{ m}^2/\text{s}$)	4.60	7.30	0.372	0.412	0.0194	0.0261

Table S5. Membrane diffusivity, D_i^m , of different counterions in Fumasep FKS and the corresponding terms to determine D_i^m .

Fumasep FKS	Counterion					
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	La ³⁺
Membrane resistivity, ρ^m ($\Omega \cdot \text{cm}$)	264 ± 2	202 ± 9	1,425 ± 87	1,670 ± 20	34,677 $\pm 2,484$	59,807 $\pm 2,692$
Conductivity measured, σ^m , $1 / \rho^m$ (S/m)	0.379	0.496	0.0702	0.0599	0.00288	0.00167
Counterion conductivity, σ_i^m , $\sigma^m t_{ct}^m$ (S/m)	0.375	0.480	0.0661	0.0569	0.00255	0.00144
Volume fraction of water, f_w , $\frac{SD / \rho_w}{SD / \rho_w + \rho_p^{-1}}$ (-)	0.252	0.191	0.235	0.226	0.216	0.231
Fixed charge density, c_{fix}^m , $\text{IEC} \cdot \rho_p (1 - f_w)$ (eq/L)	1.63	1.76	1.67	1.69	1.71	1.68
Membrane diffusivity, D_i^m , $\frac{R_g T \sigma_i^m}{F^2 z_i z_{\text{fix}} c_{\text{fix}}^m}$ ($10^{-11} \text{ m}^2/\text{s}$)	6.11	7.25	0.527	0.448	0.0132	0.00760

Table S6. Membrane diffusivity, D_i^m , of different counterions in Ralex CMHPES and the corresponding terms to determine D_i^m .

Ralex CMHPES	Counterion					
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	La ³⁺
Membrane resistivity, ρ^m ($\Omega \cdot \text{cm}$)	247 ± 33	310 ± 56	1,036 ± 476	966 ± 155	2,065 ± 23	5,241 ± 621
Conductivity measured, σ^m , $1 / \rho^m$ (S/m)	0.404	0.323	0.0965	0.104	0.0484	0.0191
Counterion conductivity, σ_i^m , $\sigma^m t_{ct}^m$ (S/m)	0.391	0.308	0.0891	0.0965	0.0395	0.0151
Volume fraction of water, f_w , $\frac{SD / \rho_w}{SD / \rho_w + \rho_p^{-1}}$ (-)	0.353	0.296	0.332	0.332	0.317	0.312
Fixed charge density, c_{fix}^m , $\text{IEC} \cdot \rho_p (1 - f_w)$ (eq/L)	1.64	1.79	1.70	1.70	1.74	1.75
Membrane diffusivity, D_i^m , $\frac{R_g T \sigma_i^m}{F^2 z_i z_{\text{fix}} c_{\text{fix}}^m}$ ($10^{-11} \text{ m}^2/\text{s}$)	6.33	4.59	0.698	0.757	0.202	0.0766

Table S7. Membrane diffusivity, D_i^m , of different counterions in Selemion AMV and the corresponding terms to determine D_i^m .

Selemion AMV	Counterion					
	Cl ⁻	Br ⁻	NO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	PO ₄ ³⁻
Membrane resistivity, ρ^m ($\Omega \cdot \text{cm}$)	268 ± 7	468 ± 29	349 ± 9	266 ± 8	463 ± 33	472 ± 94
Conductivity measured, σ^m , $1/\rho^m$ (S/m)	0.373	0.214	0.287	0.376	0.216	0.212
Counterion conductivity, σ_i^m , $\sigma^m t_{ct}^m$ (S/m)	0.353	0.205	0.267	0.328	0.180	0.159
Volume fraction of water, f_w , $\frac{SD/\rho_w}{SD/\rho_w + \rho_p^{-1}}$ (-)	0.183	0.154	0.171	0.264	0.197	0.229
Fixed charge density, c_{fix}^m , $\text{IEC} \cdot \rho_p (1 - f_w)$ (eq/L)	1.94	2.01	1.97	1.75	1.91	1.83
Membrane diffusivity, D_i^m , $\frac{R_g T \sigma_i^m}{F^2 z_i z_{\text{fix}} c_{\text{fix}}^m}$ ($10^{-11} \text{ m}^2/\text{s}$)	4.84	2.71	3.60	2.50	1.26	0.771

Dielectric Constant

As discussed in the main manuscript, effective dielectric constants obtained from analyses of the transport model, ϵ_r , are generally larger than experimental dielectric relaxation spectroscopy (DRS) measurements, ϵ_{DRS} , as summarized in Table S8. The measured volume fractions of water, averaged across the different counterion, are also listed.

Table S8. Averaged volume fractions of water, f_w , dielectric constants from regression analyses, ϵ_r , and dielectric constants from DRS measurements, ϵ_{DRS} , of the four membranes investigated in this study.

	Selemion CMV	Fumasep FKS	Ralex CMHPES	Selemion AMV
f_w (-)	0.263	0.225	0.323	0.200
Effective dielectric constant from model, ϵ_r (-)	63	51	74	105
DRS dielectric constant, ϵ_{DRS} (-)	3.7 ± 0.3	3.2 ± 0.2	7.7 ± 0.9	4.2 ± 0.3

We postulate that ϵ_r should reflect the dielectric property of the local environment experienced by the migrating counterions. Hence, the value would more closely resemble the dielectric constant of pore water in the free volume of the IEMs. On the other hand, the dielectric constant determined using DRS gives the bulk permittivity of the entire hydrated membrane matrix. Thus, ϵ_{DRS} includes contributions from both water and polymer phases. To further examine the plausibility of this explanation, we use the Maxwell-Garnett equation for the effective medium approximations. Considering water as the discontinuous phase (i.e., lower volume contribution to the composite matrix), the Maxwell-Garnett equation is^{13,14}

$$\frac{\epsilon_m - \epsilon_p}{\epsilon_m + 2\epsilon_p} = f_w \frac{\epsilon_w - \epsilon_p}{\epsilon_w + 2\epsilon_p} \quad (\text{S21})$$

Rearranging the equation to express ϵ_w in terms of other parameters yields

$$\epsilon_w = \frac{(f_w + 2)\epsilon_m + (2f_w - 2)\epsilon_p}{(f_w - 1)\epsilon_m + (2f_w + 1)\epsilon_p} \epsilon_p \quad (\text{S22})$$

Using experimentally-determined values of ε_m and f_w (DRS and SD, respectively), eq S22 can be employed to examine the relationship between polymer and water dielectric constants. Utilizing the values of Ralex CMHPES as an example, Figure S1 shows the water phase dielectric constant as a function of polymer dielectric constant.

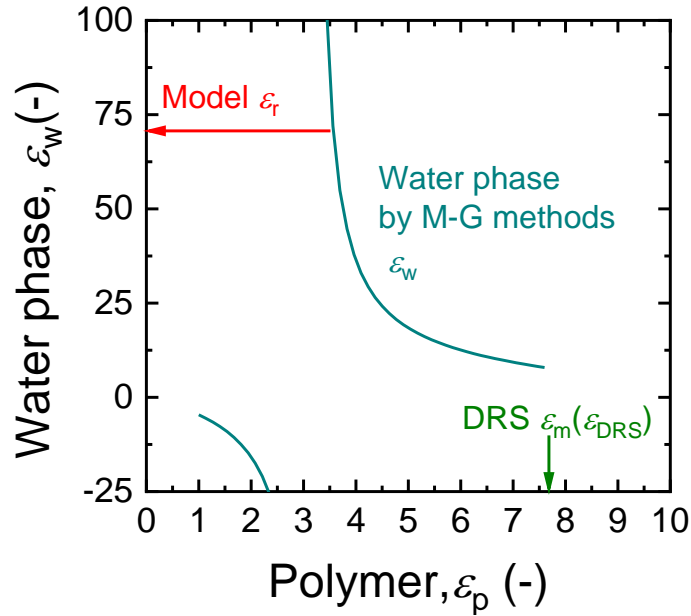


Figure S1. Water phase dielectric constant, ε_w , as a function of dry polymer dielectric constant, ε_p , to obtain the experimental ε_m value determined with DRS for Ralex CMHPES, according to the Maxwell-Garnett equation. f_w used in the calculations is from SD data from gravimetric experiments. ε_m is marked by the green arrow, whereas the red arrow denotes the effective dielectric constant from the regression analysis of the transport model.

According to the Maxwell-Garnett equation for effective medium approximations, the polymer phase dielectric constant is around 3.6 for the water phase dielectric constant to match with the value from regression analysis of the transport model. This ε_p is within the range for dry polymers reported in literature. However, because the relationship between ε_w and ε_p slopes very steeply around the region of interest, extremely precise measurements of ε_p , ε_m and f_w are needed to accurately determine ε_w using this approach. Therefore, unavoidable uncertainties in experimental measurements would propagate into the model and be amplified, potentially

producing huge inaccuracies in the model outputs. Thus, while this method to experimentally characterize the dielectric constant of the local water environment within IEMs is theoretically viable, the practical execution of the procedure is likely to be technically very challenging.

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