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Theory of Multicomponent Phenomena in Cation-Exchange Membranes: Part II. Transport Model and Validation

Andrew R. Crothers,1,2,* Robert M. Darling,3,*** Ahmet Kusoglu,2,*** Clayton J. Radke,1,4 and Adam Z. Weber2,***

1Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, United States of America
2Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States of America
3United Technologies Research Center, East Hartford, Connecticut 06108, United States of America
4Earth Sciences Division, Lawrence Berkeley National Laboratory, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States of America

Multicomponent mass-transport in cation-exchange membranes involves the movement of multiple species whose motion is coupled one to another. This phenomenon mediates the performance of numerous electrochemical and water purification technologies. This work presents and validates against experiment a mathematical model for multicomponent mass transport in phase-separated cation-exchange membranes (e.g., perfluorinated sulfonic-acid ionomers). Stefan-Maxwell-Onsager theory describes concentrated-solution transport. Hydrodynamic theory provides constitutive relations for the solute/solvent, solute/membrane, and solvent/membrane friction coefficients. Classical porous-medium theories scale membrane tortuosity. Electrostatic relaxation creates friction between ions. The model uses calculated ion and solvent partitioning between the external solution and the membrane from Part I of this series and incorporates the corresponding ion speciation into the transport coefficients. The proposed transport model compares favorably to properties (e.g., membrane conductivity, transference numbers, electroosmosis, and permeability) measured in dilute and concentrated aqueous binary and ternary electrolytes. The results reveal that the concentration and type of ions in the external solution alter the solvent volume fraction and viscosity in the hydrophilic pathways of the membrane, changing macroscale ionomer conductivity, permeability, and transference numbers. This work provides a physicochemical framework to predict ion-exchange-membrane performance in multicomponent systems exhibiting coupled transport.

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Supplementary material for this article is available online.

List of symbols

**Roman

\[ V_i \quad \text{Partial molar volume of species } i, \text{ m}^3 \text{ mol}^{-1} \]

\[ \bar{V}_i \quad \text{Effective molar viscous volume of species } i, \text{ m}^3 \text{ mol}^{-1} \]

\[ K_{ij} \quad \text{Friction coefficient between species } i \text{ and } j, \text{ J s}^{-1} \]

\[ L_{i,j}^{\text{trans,0}} \quad \text{Membrane solvent transmissibility, m}^2 \text{ J}^{-1} \text{ s}^{-1} \]

\[ M_i \quad \text{Molar mass of species } i, \text{ g mol}^{-1} \]

\[ M_{ij}^M \quad \text{Components } i \text{ and } j \text{ of matrix } M^M \text{ between species, } J \text{ cm}^{-5} \]

\[ R_0 \quad \text{Radius of water molecule, 0.1375 nm} \]

\[ R_{\text{effective}} \quad \text{Effective radius of hydrophilic pore accessible to hydrated ions, m} \]

\[ R_{\text{pore}} \quad \text{Pore radius, nm} \]

\[ c_i \quad \text{Molar concentration of species } i, \text{ mol dm}^{-3} \]

\[ f_{ij} \quad \text{Association fraction of species } i \text{ into species } j \]

\[ m_i \quad \text{Molarity of species } i, \text{ mol kg}^{-1} \text{ solvent} \]

\[ n_i \quad \text{Moles of species } i, \text{ mol} \]

\[ z_i \quad \text{Charge number of species } i \]

\[ \lambda_i \quad \text{Hydrodynamic friction coefficient of species } i \text{ in the membrane, J s}^{-5} \]

\[ D_{ij} \quad \text{Diffusion coefficient between species } i \text{ and } j, \text{ m}^2 \text{ s}^{-1} \]

\[ F \quad \text{Faraday’s constant, 96,487 C mol}^{-1} \]

\[ G \quad \text{Domain geometric factor} \]

\[ I \quad \text{Ionic strength, mol m}^{-3} \]

\[ N \quad \text{Number of species} \]

\[ R \quad \text{Gas constant, 8.3145 J mole}^{-1} \text{ K}^{-1} \]

\[ T \quad \text{Temperature, 298 K} \]

\[ k \quad \text{Inverse Debye length, m}^{-1} \]

\[ \mu \quad \text{membrane thickness, m} \]

\[ p \quad \text{Pressure, Pa} \]

**Greek

\[ \varepsilon_0 \quad \text{Vacuum permittivity, 8.85 \times 10^{-12} F \text{ m}^{-1}} \]

\[ \varepsilon_r \quad \text{Relative dielectric constant} \]

\[ \theta_i \quad \text{Distribution factor for species } i \text{ in a hydrophilic domain} \]

\[ \psi_i \quad \text{Electrochemical potential of species } i \text{ relative to that of species } n, \text{ J mol}^{-1} \]

\[ \beta \quad \text{Ratio of the effective pore radius and the true pore radius} \]

\[ \eta \quad \text{Solution viscosity, Pa s} \]

\[ \kappa \quad \text{Conductivity, S cm}^{-1} \]

*Electrochemical Society Student Member.
**Electrochemical Society Member.
***Electrochemical Society Fellow.
*E-mail: acrothers@lbl.gov

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[1675-1678]
Transport of multiple ions in phase-separated, solvent-filled membranes dictates performance of numerous energy-storage and conversion devices. For example, recent advances in proton-exchange-membrane (PEM) fuel cells involve new catalyst alloys and cerium additives that increase kinetic performance and durability but introduce challenges related to multi-ion transport in the cation-exchange membrane. Similarly, low-temperature PEM electrolysistem technologies have recently received intense interest, but the involved products and reactants can transport across the membrane. Membranes in redox-flow batteries (RFBs) absorb and transport numerous redox-active and supporting-electrolyte species. Often, these devices operate in aqueous environments and use perfluorinated sulfonic-acid (PFSA) ionomers as separators. Multicomponent transport in these materials faces the conflicting goals of promoting movement of current-carrying ions between the anode and cathode while preventing crossover of redox-active species or contaminants that decrease device performance. Although previous literature provides useful descriptions of transport in these membranes, multi-ion transport and thermodynamics remain poorly understood.

There are two general approaches for mass-transport in ion-exchange membranes. In the limiting regime of negligible ion and water concentrations in the membrane, dilute-solution theory is valid. Dilute-solution theory predicts that the flux of a species $i$ is proportional to the concentration gradient of $i$ plus the force an electric field applies to $i$. This theory predicts that the number of transport coefficients (e.g., Fickian diffusion coefficients) scales by the number of mobile species in the membrane (i.e., $N - 1$ where $N$ is the total number of species present, including mobile species and the membrane). The dilute-solution theory approach has the benefit of being relatively simple to use and understand. It also requires relatively few experiments to characterize fully all transport properties. Unfortunately, dilute-solution theory cannot describe numerous transport phenomena exhibited by ion-exchange membranes, including electroosmosis (the transport of water under an applied electric field), the flow of ions due to a water concentration gradient, and, generally, the flux of species $i$ due to a concentration gradient of species $j$. As a result, measured dilute-solution diffusion coefficients in concentrated solutions are not solely properties of the material. Rather, they are effective coefficients valid only for the operating conditions for which they are measured.

The second approach is concentrated-solution theory. This formalism is more general and is applicable to solutions that range from highly concentrated to the dilute limit, in which case it reduces to dilute-solution theory. Concentrated-solution theory predicts that the flux of species $i$ is a linear function of the electrochemical potential gradient of all but one species $j$ present. Concentrated-solution theory is the general instantiation of classical nonequilibrium thermodynamics for multicomponent solutions. It naturally describes the coupling between forces on species $j$ and transport of species $i$. The number of independent transport coefficients in concentrated-solution theory (e.g., binary diffusion coefficients) scales as $(N - 1)/N$, as it should in real systems. Dilute-solution theory, therefore, contains an insufficient number of transport parameters. An unfortunate consequence of a concentrated-solution description is the introduction of a large number of parameters for multicomponent systems. For example, a typical vanadium RFB with eight species necessitates 28 different experiments to characterize the transport properties completely. Further, these transport coefficients are strong functions of concentration and membrane properties (as with dilute-solution theory) and, therefore, must be quantified across relevant conditions.

In between the dilute and concentrated formalisms, there are compromise theories that incorporate certain but not all transport couplings into dilute-solution theory, such as making ion flux related to water transport or adding in electroosmosis. These models provide a promising method to predict multicomponent transport while remaining relatively simple. However, it is not clear under what conditions these simpler approaches are valid representations of the full concentrated-solution description.

Studies of multicomponent transport in ion-exchange membranes face a choice between using dilute-solution theories and neglecting relevant transport couplings or using concentrated-solution theory but introducing an intractable number of parameters. We reduce the intractability of concentrated-solution theory by providing a mathematical formalism to calculate transport parameters at the relevant conditions based on microscopic properties of the membrane. By estimating the full set of transport properties, the model reduces the burden on extensive experimental characterization.

In this paper, we use the Stefan-Maxwell-Onsager formulation to calculate transport properties. This theory is formally equivalent to other formulations of concentrated-solution theory and attributes transport coefficients to frictional interactions between species. The frictional interactions are calculable with microscale theories.
parameters mostly available from bulk-solution measurements. In the Results and Discussion section, literature data relevant for fuel-cell and RFB membranes validate the model.

**Theory**

We focus on perfluorinated sulfonic-acid (PFSA) chemistry because of its extensive characterization and widespread use. Nafion is the most widely-used type of PFSA. This polymer consists of a hydrophobic polytetrafluoroethylene backbone (PTFE) with side chains that terminate in negatively charge sulfonate groups. Upon immersion in aqueous solutions or water vapor, the domains microphase separate into water-filled, interconnected hydrophilic (“bubbles”) and hydrophobic PTFE structural domains. In this section, non-equilibrium thermodynamics is employed for multi-ion transport in the membrane structure. We provide a consistent treatment of equilibrium ionic speciation and develop a microscopic model for friction coefficients. Finally, we relate the predicted friction coefficients to macroscopic, experimentally accessible concentrated-solution transport parameters.

**Multicomponent mass-transport equations.**—Isothermal, isotropic, multicomponent mass transport is governed by the nonequilibrium thermodynamic driving force on species \( i \), \( d_i \), balancing against the drag forces between \( i \) and all other species \( j \) in the system. According to the Stefan-Maxwell-Onsager theory,\(^{13,25,29}\)

\[
\begin{equation}
\begin{aligned}
d_i &= \sum_{j=1}^{N} K_{ij}(\nu_j - \nu_i)
\end{aligned}
\end{equation}
\]

where \( K_{ij} \) characterizes the friction between species \( i \) and \( j \) and \( \nu_i \) is the velocity of species \( i \). The driving force for transport is\(^ {29}\)

\[
\begin{equation}
\begin{aligned}
d_i &= c_i \left( \nabla \mu_i - \frac{M_i}{\rho} \nabla p + X_i + \frac{M_j}{\rho} \sum_j X_j c_j \right)
\end{aligned}
\end{equation}
\]

where \( c_i \), \( \mu_i \), \( M_i \), and \( X_i \) are, respectively, the concentration (defined later), electrochemical potential, molar mass, and external body force on species \( i \); \( p \) is pressure, and \( \rho \) is mass density. We account for electrostatic forces in the electrochemical potential \( \mu_i \) rather than in a body force \( X_i \). The membrane, species \( M_i \), is affixed to a support (e.g., a mesh or gasket) that imparts a pinning force \( X_M \). A force balance on the membrane dictates that this force is equal to the pressure in the membrane, \( \nabla p = c_M X_M \). An explicit stress balance in the membrane specifies \( X_M \).\(^ {20,29}\) Absent other external forces, substitution of Eq. 2 into Eq. 1 for each mobile species \( i \) in the membrane relates the electrochemical potential gradients to species velocities\(^{13,25,29}\)

\[
\begin{equation}
\begin{aligned}
c_i \nabla \mu_i &= K\bar{M}_i(-\nu_i) + \sum_{j=1}^{N} K_{ij}(\nu_j - \nu_i)
\end{aligned}
\end{equation}
\]

For \( i = M \), isothermal Gibbs–Duhem demands that

\[
\begin{equation}
\begin{aligned}
c_M \nabla \mu_M &= \nabla p = \sum_{i=M} K_{iM} \nu_i
\end{aligned}
\end{equation}
\]

where \( \nu_i \) is a superficial velocity and \( K_{ij} \) is the friction coefficient between species \( i \) and \( j \). The electrochemical potential is a function of composition, pressure, temperature, \( T \), and electric state. The pressure gradient appears in Eq. 4 but not in Eq. 3 because of the pinning force on the membrane.\(^ {32,45,46}\) In Eqs. 3 and 4, the reference velocity is that of the membrane (i.e., \( \nu_M = 0 \)). Conservation of the membrane mass provides an additional constraint that relates \( \nu_M \) to the laboratory frame of reference (i.e., to the support that affixes the membrane).\(^ {37}\) At steady state, the membrane is not actively swelling and the membrane velocity equals the velocity of the laboratory frame-of-reference with a superscript of the reference species (i.e., \( M \)). If the species are chemically independent (i.e., no reactions between them; the proceeding section lifts this restriction), then for \( N \) species (including all species absorbed in the membrane and the membrane), there are \( N - 1 \) independent equations of this form.\(^ {29}\) Eq. 3 in matrix form is\(^ {13}\)

\[
\begin{equation}
\begin{aligned}
D &= M^{M'V}
\end{aligned}
\end{equation}
\]

where \( D \) and \( V \) are \( N - 1 \) by 3 matrices in which the \( i \)th row contains, respectively, the components of the 3D vector of driving forces and velocities of species \( i \) (i.e. \( D_{i} = c_i \nabla \mu_i \) and \( V_i = \nu_i \)), where the subscript \( i \) denotes a row excluding the row and column \( M \), due to linear dependence.\(^ {39}\) The transport coefficient matrix \( M^{M'} \) is \( N - 1 \) by \( N - 1 \) where \( M_{ij}^{M} = K_{ij} \) for \( i = j \) and \( M_{ij}^{M} = -\sum_{k=1}^{N} K_{ik} \).

Onsager reciprocal relations dictate that the friction coefficients are symmetric, \( K_{ij} = K_{ji} \).\(^ {38,40}\) Consequently, there are \( N(N - 1)/2 \) friction coefficients. \( K_{ij} \) coefficients are related to binary interspecies diffusion coefficients according to\(^ {25}\)

\[
\begin{equation}
\begin{aligned}
\mathcal{D}_{ij} &= \frac{RTc_\mathcal{C}c_i}{K_{ij}c_i}
\end{aligned}
\end{equation}
\]

where \( c_i \) is the total molar concentration of the solution.

The molar concentration for a phase-separated membrane is defined either on a superficial basis (e.g., a homogenous phase) that includes the polymer volume \( c_p = n_i/\sum_i n_i \nu_i \), where \( n_i \) and \( \nu_i \) are the molar and partial molar volume of species \( i \), or an interstitial basis (e.g., heterogeneous phases) that only includes the electrolyte solution in the membrane pores \( c_i = n_i/\sum_i n_i \nu_i \). We use the latter definition because it is more amenable to microscopic theories of \( \mathcal{D}_{ij} \) that are derived for bulk electrolyte solutions or porous media. We neglect changes to the total molar concentration \( c_i \) in the hydrophilic domains; the molar concentration of species \( i \) is \( c_i = c_i(n_i/\sum_i n_i \nu_i) \) where \( c_i \) is set to the molar concentration of salt-free water at 25 °C, \( (\approx 55.2 \text{ mol dm}^{-3}) \). This assumption is rigorously valid for high water contents (\( \lambda > 10 \)) or for membranes exchanged with cations that have molar volumes similar to water.

**Transport with ion association.**—Many ionic species undergo ion-pair or acid-base equilibria that alter transport properties.\(^ {49}\) Transport measurements typically control amounts of neutral components added to the system and treat the \( N \) constituent ionic species as fully dissociated in solution (we call this the “Experimental Construct” and denote quantities in the construct with superscript exp). For example, sulfuric acid is treated as protons and sulfate ions. The Experimental Construct provides independent driving forces and fluxes for species. However, because friction between species depends on size and charge, microscopic models consider \( N^\text{mol} \) species in their actual, associated states (we call this the “Molecular Construct” and denote quantities in this construct with superscript mol). For example, sulfuric acid is treated as protons, bisulfate, and sulfate ions.\(^ {32}\)

By accounting for how driving forces in the Molecular Construct are interdependent, Appendix A shows that the friction-coefficient matrix in the Molecular Construct, \( M^{M^\text{mol}} \) (a \( N^\text{mol} - 1 \) by \( N^\text{mol} - 1 \) matrix), is related to friction coefficients in the Experimental Construct, \( M^{\text{exp}} \) according to

\[
\begin{equation}
\begin{aligned}
M^{M^\text{mol}} &= (F [M^{M^\text{mol}}]^{-1} F')^{-1}
\end{aligned}
\end{equation}
\]

where \( F \) is a \( N - 1 \) by \( N^\text{mol} - 1 \) matrix with \( i, j \) entries \( f_{ij} \), and \( f_{ij} \) is the fraction of moles of species \( i \) in the Experimental Construct, \( n_i^\text{exp} \), that partially associates into \( n_i^\text{mol} \) moles of species \( j \) in the Molecular Construct

\[
\begin{equation}
\begin{aligned}
f_{ij} = \frac{n_i^\text{mol} s_j}{n_i^\text{exp} s_j}
\end{aligned}
\end{equation}
\]

Here, \( s_i \) and \( s_j \) are the stoichiometric coefficients of species \( i \) and \( j \), respectively, in the reaction of \( i \) associating with another species.
to form \( f \). For example, protons (species \( i \)) associating with sulfite ions to form bisulfite ions (species \( j \)). Note that \( f_i = 1 \). Theory gives that the Molecular Construct transport coefficients (e.g., \( M^n \)) to calculate the Molecular Construct transport coefficients (e.g., \( M^n \)). In that case, \( M^n \) provides \( \mathbf{D}_{\text{eff}} \) according to the definition of \( M^n \). For convenience, we drop the superscript \( \exp \) outside this section for quantities in the experimental construct.

**Friction coefficients.**—In a liquid solution consisting of solvent and ionic species in a membrane, there are six types of friction coefficients: ion/solvent, cation/anion, cationcation, anion/anion, ion/membrane, and solvent/membrane. A hydrodynamic model of membrane pores gives ion/membrane and solvent/membrane friction coefficients. The transport coefficients are scaled by the tortuosity \( \tau \) and volume fraction, \( \omega \), of the hydrophilic membrane domains to relate the transport coefficients of a single hydrophilic domain to effective, superficial membrane fluxes used in Eqs. 3 and 4.

Tortuosity scales according to Arche’s law, \( \tau = (1 - \omega \delta)_\text{t} \), where \( \omega \) is the tortuosity scaling parameter, \( \delta \) is the volume fraction of the polymer backbone, \( \nu = \frac{n + \nu}{6} \) neglecting the volume of absorbed ions in the membrane), \( \nu = \frac{n}{6} \) is the partial molar volume of polymer per charged group (=523.8 cm\(^3\)/mol-\( \text{SO}_4 \) for Nafion). \( \chi \) is independent of water content and electrolyte concentration in the membrane.

**Ion/solvent and ion ion friction coefficients.**—For ion/solvent friction coefficients, the Stokes–Einstein equation predicts the changes with solution viscosity of the binary diffusion coefficient as a result of the drag of an ion, idealized as a sphere, moving (or rotating) through a stagnant continuum solvent:

\[
\mathbf{D}_{\text{sol}}^i = \left(1 - \frac{\phi}{\tau}\right) \frac{n}{\eta} \mathbf{D}_{\text{sol}}^i \quad \eta = \frac{n}{\nu \eta} \left(1 - \sum_{i=0}^{N^\text{mol}} \frac{\mu^m_i \nu_i}{2}ight) \quad \left(1 - \sum_{i=0}^{N^\text{mol}} \frac{\mu^m_i \nu_i}{2}\right)^2
\]

where \( \eta \) is the solution viscosity and the superscript \( \infty \) denotes infinite dilution. The term in parenthesis on the right side corrects the interstitial diffusion coefficient for the tortuosity and volume fraction of hydrophilic channels. The viscosity ratio arise because the solution becomes more viscous at high ion strengths due to increased steric interactions between ions in solution. Einstein’s viscosity equation predicts how solution viscosity changes with concentration:

\[
\eta = \frac{1}{2} \left(1 + \sum_{i=0}^{N^\text{mol}} \mu^m_i \nu_i \frac{n}{2}ight) \left(1 - \sum_{i=0}^{N^\text{mol}} \mu^m_i \nu_i \frac{n}{2}\right)^2
\]

where \( \mu_i \) is the effective molar viscous volume of species \( i \), that is fit to electrolyte-solution viscosity data. Stokes–Einstein theory (Eq. 9) is widely used and generally effective at predicting the concentration dependence of ion-solvent diffusion coefficients, although agreement with experiment is imperfect. In particular, Stokes–Einstein theory is inaccurate for associating electrolytes, corrections of which are accounted for by using the Molecular Construct.

Although local viscous interactions govern ion/solvent friction, long-range electrostatics dominate ion/ion interactions. A “cloud” of mostly oppositely charged ions surrounds an ion in solution. When an external field is applied, that cloud distorts and exerts a retarding force on the ion opposing the external field. From this resistive force, Debye–Hückel-Onsager theory predicts that in binary electrolytes the diffusion coefficient for oppositely charged ions varies with the square-root of concentration.

\[
\mathbf{D}_{\text{sol}}^i \propto \left(1 - \frac{\phi}{\tau}\right) \sqrt{\frac{\eta}{\eta_0}} \quad \text{for} \quad z_i = M_0 \theta_i = 0 < 0
\]

where \( \eta_0 \) is the Molecular Construct ionic strength (=\( \sum_{i=0}^{N^\text{mol}} c_i \)). Eq. 11 relates diffusion coefficients measured in bulk solution at a given ionic strength to those at other concentrations. Chapman and Wesselingh et al. suggested that, since the Debye–Hückel ion cloud is governed by the ionic strength in multicomponent electrolytes; Eq. 11 also applies to mixtures. Experiments agree with the Debye–Hückel-Onsager description that friction between similarly charged ions is negligible as they scarcely interact, or

\[
\mathbf{D}_{\text{sol}}^i \propto \left(1 - \frac{\phi}{\tau}\right) \sqrt{\frac{\eta}{\eta_0}} \quad \text{for} \quad z_i = M_0 \theta_i = 0 > 0
\]

**Ion and solvent/membrane friction coefficients.**—Debye–Hückel–Onsager theory does not apply to ionic groups attached to the polymer membrane, since they are fixed and unable to form an ionic cloud around mobile ions. Still, the membrane exerts a frictional force on aqueous ions and solvent from microscale-viscous interactions with the membrane walls. Microscale hydrodynamics predicts viscous interactions between a fluid and a solid wall. Species velocities and concentrations discussed up to this point are macroscopic averages and correspond to experimentally measurable quantities. In developing a microscale hydrodynamic model, we invoke microscopic, local quantities that are not experimentally accessible and are denoted with a superscript \( \text{loc.} \).

Appendix B shows that the area-averaged, superficial velocity \( v_z \) through the membrane (through-direction denoted as the \( z \)-coordinate) where each mobile species is under an electrochemical potential gradient \( \partial h_i / \partial z \) is

\[
v_z = -\sum_{i=M}^{N^\text{mol}} \frac{\mu^m_i}{H^i} \frac{\partial h_i}{\partial z}
\]

where \( H^i \) is a hydrodynamic friction coefficient that satisfies the creeping-flow momentum balance in a pore with appropriate boundary conditions. By definition, \( v_z \) is the sum of species velocities in the Molecular Construct \( v_z^\text{M} \) weighted by their mass fractions \( w_i^\text{M} \) (i.e., mass-averaged velocity, \( v_z = \sum_{i=M}^{N^\text{mol}} w_i^\text{M} \)) where \( w_i^\text{M} = n_i^\text{M} M_i / \sum_{j=M}^{N^\text{mol}} n_j^\text{M} M_j \). In Appendix C, we demonstrate that the expression for \( K^\text{M}_i \) that satisfies both the hydrodynamic prediction of Eq. 13 and frictional interactions in Eq. 3 is

\[
K^\text{M}_i = w_i^\text{M} H^i + \sum_{j=M}^{N^\text{mol}} K^j \left( H^j / H^i = 1 \right)
\]

where the first term on the right is due to hydrodynamic interactions directly causing friction on species \( i \) and the second term is due to hydrodynamic friction on species \( j \) that, in turn, exerts friction \( K^\text{M}_j \) on \( i \).

Following classic treatments of electrosketics in microchannels, Appendix B shows that for a translationally invariant pore forming a channel with tortuosity \( \tau \), \( H^i \) is

\[
H^i = 4G \eta \left( \frac{\tau}{R^\text{M}} \right) \left( 1 - \frac{\phi}{\tau} \right)
\]

where \( R^\text{M} \) is the radius of the pore and is a function of the membrane polymer volume fraction, \( R^\text{M} = d_0 \phi M_0 (1 - \phi M)_1/2 / 2 \), \( d_0 \) is dry-membrane domain spacing (2.7 nm for Nafion) and \( n \) is a swelling
parameter determined from microstructural characterization (1.33 for Nafion).\textsuperscript{2} \(G\) is the semi-empirical geometric factor that accounts for pore shape and distribution of sizes of the hydrophilic channels, and is independent of membrane water content and ion concentration.\textsuperscript{53} Just as in Eqs. 9 and 11, the term in parenthesis on the right side corrects the interstitial hydrodynamic coefficient for the tortuosity and volume fraction of hydrophilic channels. \(\theta_i\) accounts for how species \(i\) distributes across the channel and equals unity when \(i\) is uniformly distributed.

To establish \(\theta_i\), we treat the negatively charged polymer sulfonate groups as uniformly distributed along the channel walls. Because cations are solvated, they cannot approach the walls closer than their solvated radius (i.e., the outer Helmholtz plane),\textsuperscript{50} which we set to the diameter of a water molecule 2\(\sigma_w = 0.275\) nm.\textsuperscript{61} Because this study deals with high membrane hydration levels where cations are fully solvated, we do not consider cation-membrane ion-pair formation (i.e., ions complexed with the surface by dehydrating and moving to the inner Helmholtz plane).\textsuperscript{60} Consequently, ionic species are distributed across a pore of effective radius \(R_{\text{pore}} = 2R_0\) according to the linearized Poisson-Boltzmann equation.\textsuperscript{60} For this system, Appendix B shows that \(\theta_i\) is given by

\[
\theta_{i=0} = \beta^2 \left( 2 - \beta^2 - z_i \theta \right)^2 + 8 \frac{4 \beta \theta (R_{\text{pore}} k^2)}{R_{\text{pore}} k I (R_{\text{pore}} k^2)} \right]
\]  

where \(\beta\) is the ratio of the effective pore radius traversed by ions after accounting for solvation and the true radius \(R_{\text{pore}} = 2R_0\). \(\theta\) is a Debye length \((=\sum_{i, j=1}^{\infty} \frac{n_i^{\text{mol}} e_i^2}{\varepsilon_\nu \nu_0 RT})^{1/2}\), \(\varepsilon_\nu\) is bulk solvent dielectric constant (= 78.3), \(\nu_0\) is vacuum permittivity, and \(I_0\) and \(I_1\) are modified Bessel functions of the first kind with order 0 and 1, respectively. We neglect changes in solvent concentration across the pore so that \(\theta_{i=0} = 1\).

Macrosopic transport coefficients.—Equations 3 and 4 provide a microscopic description of multi-ion transport in membranes that relate species fluxes to driving forces, whereas experiments obey a macroscopic description in which experimentally controlled driving forces cause species fluxes. Fuller showed that Eq. 5 inverts to a macroscopic form\textsuperscript{32}

\[
N_i = - \sum_{j=M} L_{ij}^{\text{M}} c_j \nabla \mu_j \]  

where \(N_i\) is the molar flux vector of species \(i \equiv M\) and \(L_{ij}^{\text{M}}\) is a component of the \(N - 1\) by \(N - 1\) symmetric matrix \(L^{\text{M}}\) defined as\textsuperscript{32,53}

\[
L^{\text{M}} = -(M^{\text{M}})^{-1} \]  

where the membrane, species M, is used as a reference.

Because experimental measurements rarely ascertain the \(L_{ij}^{\text{M}}\) transport coefficients directly, we rewrite Eq. 17 in terms of transport coefficients that are measureable under well-defined experimental conditions, such that in terms of a controlled gradient of electrochemical potential \(\mu_{j,n}\)\textsuperscript{13,25}

\[
N_i = t_{j,n}^{\text{M}} \nabla \mu_{j,n} - \sum_{j=M} L_{ij}^{\text{M}} t_{j,n}^{\text{M}} \frac{1}{z_i F^2} \nabla \mu_{j,n} \]  

or, equivalently, in terms of a controlled current density

\[
N_i = t_i^{\text{M}} \nabla \mu_{j,n} - \sum_{j=M} \alpha_{ij}^{\text{M}} \nabla \mu_{j,n} \]  

where \(F\) is Faraday’s constant, \(z_i\) is the charge number of species \(i\), \(t_i^{\text{M}}\) is the transference number of species \(i\), \(\kappa\) is conductivity, and \(\alpha_{ij}^{\text{M}}\) is the transport coefficient between species \(i\) and \(j\). In the absence of concentration, pressure, or temperature gradients, for a charged species \(i\), \(\nabla \mu_i = z_i F \nabla \Phi\), where \(\Phi\) is the electric potential. To avoid invoking an arbitrary definition of \(\nabla \Phi\) when there are concentration gradients, Eqs. 19 and 20 use \(\mu_{j,n}\), the chemical potential of species \(i\) relative to that of species \(n\), \(\mu_{i,n} = \mu_i - z_i \mu_n\). \(\mu_{j,n}\) is independent of \(\Phi\), depending only on the thermodynamic variables pressure, concentration, and temperature.\textsuperscript{25} The first terms on the right sides of Eqs. 19 and 20 specify flux due to concentration and pressure gradients and the second terms specify transport due to migration. Because protons are present in numerous applications of cation-exchange, a convenient choice for \(n\) is \(H^+\).\textsuperscript{13}

Equations 19 and 20 are general for isothermal transport. The transport coefficients appearing in these equations are related to the \(L_{ij}^{\text{M}}\)s and are material properties of the polymer membrane that for a set composition and temperature are independent of the applied driving forces. Under certain common experimental conditions, these properties have a clear physical interpretation. Specifically, ionic conductivity, \(\kappa\), and \(N - 2\) transference numbers, \(t_{ij}^{\text{M}}\), relate the fluxes and current to the applied electric potential in the absence of concentration, temperature and pressure gradients

\[
i = - (\kappa) \nabla \Phi = \left( F \sum_{j=M} \sum_{j=M} L_{ij}^{\text{M}} z_i c_j \nabla \Phi \right) \]  

for \(\nabla \Phi = \nabla V = \nabla p = 0 \]  

and

\[
N_i = \left( \frac{M}{\epsilon_\nu} \right) \frac{1}{F} = \left( \frac{\alpha_i^{\text{M}}}{\epsilon_\nu} \sum_{j=M} L_{ij}^{\text{M}} z_j c_j \right) \left( \frac{1}{F} \right) \]  

for \(\nabla c_j = \nabla V = \nabla p = 0 \]  

where the second equality provides \(\kappa\) and \(t_{ij}^{\text{M}}\) in terms of the \(L_{ij}^{\text{M}}\)s. The electroosmotic coefficient is related to the transference number of water by the ratio \(t_{ij}^{\text{M}} / z_j = \xi_j\), which is finite even though \(z_0 = 0\).\textsuperscript{13} Similarly, \(\alpha_{ij}^{\text{M}}\) has a straightforward physical interpretation for experiments in the absence of current; \(\alpha_{ij}^{\text{M}}\) is the proportionality constant relating species fluxes under chemical potential gradients absent net ionic current (i = 0) and relate to \(L_{ij}^{\text{M}}\) according to\textsuperscript{13}

\[
N_i = - \alpha_{ij}^{\text{M}} \nabla \mu_{j,n} = \left( L_{ij}^{\text{M}} c_j \frac{t_{ij}^{\text{M}}}{z_j z_i F^2} \right) \nabla \mu_{j,n} \]  

for \(i = 0 \]  

where \(\alpha_{ij}^{\text{M}}\) is symmetric, which gives \((N - 1)N/2\) \(\alpha_{ij}^{\text{M}}\)s of which \((N - 2)(N - 1)/2\) are independent.

The transmissibility of the membrane to water, \(L_{\text{trans,0}}\), dictates the superficial velocity of water through the membrane under an applied pressure gradient. The solvent/solvent transport coefficient, \(\alpha_{00}\), relates to measured \(L_{\text{trans,0}}\) as\textsuperscript{13}

\[
L_{\text{trans,0}} \approx \alpha_{00} \frac{\nu_0^2}{l} \]  

where the membrane thickness, \(l\), increases with water content from the dry thickness, \(l^0\); for isotropic swelling \(l = l^0 \left( 1 + \frac{m}{\rho_0 \nu_0} \right) \)\textsuperscript{0.7}. Equation 24 is approximate because neglects volume change on mixing of the water and membrane andneglects ionic contributions to the volume of the solution.

Parameters and Calculations.—Literature reports values of \(\kappa\) and, less frequently, \(\xi\), \(t_{ij}^{\text{M}}\), and \(L_{\text{trans,0}}\) for PSFA membranes. Here, we consider properties of membranes that are immersed in aqueous electrolyte solutions where membrane water content is relatively high. To calculate measured properties with the proposed model for a membrane in bulk solution at a given composition, we first calculate the water volume fraction \(\phi_0\) (neglecting the volume of
ions, \( \phi_0 = 1 - \phi_M \) and molality of ions in the membrane \( m_i \) and the speciation of associating ions \( f_{i,j} \) from chemical-equilibrium relations outlined in Part I. Although this calculation is self-consistent, model and experimental errors in electrolyte partitioning propagate to measurements and predictions of the transport properties. We relate the membrane composition to the chemical potentials of the external environment using an equilibrium model. In the steady state, we need not include a viscoelastic response of the polymer, which may be required in a transient simulation.

Equations 6, 9, 11, and 12 give \( K_{ji}^{M} \) for species \( i \) and \( j \) excluding the membrane \( M \) while Eq. 14 gives \( K_{M}^{M} \). The \( K_{M}^{M} \)’s specify \( M^{M} \) and Eq. 7 gives \( M^{M} \). Inversion of \( M^{M} \) following Eq. 18 provides \( M^{M} \). The components of \( L^{M} \) give measured transport properties outlined in Eqs. 21–23. Matrix inversions are performed using the Python package NumPy version 1.16.

Because of the wide availability of data, we restrict our investigation to the Nafion PFSA chemistry. Specifically, we use data for Nafion versions N117, N115, N212, and N211. The different numbered membranes have the same molecular formulae but the N11x sequence is extruded, whereas the series N21x is cast from solution; \( x \) denotes thickness in units of mils. For operating parameters, we use ambient temperature (298 K) and pressure (101.3 kPa). As discussed in Supplemental Material, measurements of bulk-solution transport provide most properties at these conditions (specifically, \( \bar{V}_i, \bar{D}_{i,j}=M, \) and \( \bar{D}_{i,j}=M,0\) at a reference concentration). Parameters of ions unavailable in the literature are set to those ions of similar charge number that are available (see SM).

Table I provides the two adjusted values for the parameters of Nafion membranes. These are Archie’s tortuosity scaling parameter, \( \chi \), and the geometric transport factor, \( G \). Results and Discussion show that the parameter values are the best eye-fit of calculated and measured membrane conductivity proton transference number, electroosmotic coefficient, and water-water transport coefficient. \( G \) and \( \chi \) are independent of membrane water and ion content. Results and Discussion compares model predictions with experiments.

Since membrane pretreatment and processing impact network tortuosity, we use two values of Archie’s parameter: \( \chi = 0.3 \) for the highly pretreated and conductive N117 and N115 membranes measured by Okada and co-workers reported to have a proton-form conductivity of \( \sim 0.2 \text{ S cm}^{-1} \) in liquid water \( 62,64 \), and \( \chi = 1.2 \) for all other datasets that consistently report \( \kappa < 0.1 \text{ S cm}^{-1} \) for proton-form membranes in liquid water at room temperature \( 65,69,70 \). Both of these values fall within the range of \( \chi \) for a range of different types of porous media \( 0.3–3.4 \). \( G \) for different pore shapes falls between 2 and 3, which correspond to circular- and slit-pore shape cross sections, respectively. This range of \( G \) is lower than the value fit here. The discrepancy is likely due an extremely heterogeneous distribution of hydrophilic domain sizes that leads to a large effective \( G \). Porous media with parallel-type pore nonuniformities in which species transport through pores that are larger than average lead to \( G \)’s that are greater than those predicted by pore shape alone.

### Results and Discussion

This section compares calculated and measured transport properties. We first consider data for membranes in dilute-aqueous solutions, partially-exchanged with proton or lithium and a monovalent cation. The external solution is sufficiently dilute so that no co-ions are present in the membrane. The absence of co-ions makes the measurements informative for fuel-cell membrane applications. These datasets also contain different transport coefficients that permit validation of various aspects of the model. We also consider membranes in concentrated external electrolytes that incorporate co-ions from the surrounding solution. Fewer transport measurements are available under these conditions, but they test model predictions when numerous species are present. Concentrated conditions are relevant for RFB operation. In particular, we calculate transport coefficients for membranes in aqueous solutions of sulfuric acid and vanadium sulfate that are representative of electrolytes in vanadium RFBs, which are the most studied flow-battery chemistry.

| Parameters | Value \([-\] | 
|------------|-------------|
| \( \chi \) | 0.3 for data from \( 62,64 \) otherwise 1.2 |
| \( G \) | 4 |

### Table I. Nafion membrane specific fitting parameters in the model.

**Figure 1.** Measured \( 63 \) (symbols) and calculated \( 62,64 \) (lines) N11x membrane (a) conductivity \( \kappa \), (b) proton transference number \( \theta_i^M \), (c) electroosmotic coefficient \( \xi \), and the transport coefficients between (d) water-water \( \alpha_{ij}^M \), (e) ion-water \( \alpha_{ij}^W \), and (f) ion-ion \( \alpha_{ij}^W \) in liquid water as function of fractional proton exchange, \( n_{H^+}/n_{SO_4^{2-}} \), with lithium (triangles), sodium (squares), potassium (pentagons), and cesium (tilted diamonds).
measured, only calculated), and (f) ion-ion transport coefficient $\alpha_{ij}^{M}$ (not measured, only calculated) as function of the fractional proton exchange $n_{H^+/HSO_4^-}$ (i.e. the fraction of negatively charged polymer sulfonate group charge-balanced by protons) with various alkali metal cations. For membranes partially exchanged with alkali cations and protons, the transport coefficients are related according to $\alpha_{iA}^{M} = -\alpha_{0i}^{M} \text{ and } \alpha_{iH^+M}^{M} = -\alpha_{A^+H^+}^{M} = \alpha_{A^+A^+}^{M}$. Best-eye fitting of the data in Fig. 1 specifies $\gamma$ and $G$, Figure S1 shows the same calculated transport properties as Fig. 1 for lithium-form membrane exchanged with other alkali cations ($\alpha_{0i}$ not measured). The fitted $\gamma$ and $G$ in Table I calculate transport properties for mixed lithium-alkali form membranes without adjustment.

Agreement in Fig. 1 between theory and experiment is sufficient for differing membrane proton fractions and ion types. There are three cases that the model differs from experiment. The model calculates a higher sodium-exchanged membrane conductivity than does the measurement. We attribute this difference to varying experimental conditions because the measured sodium-exchanged samples have lower conductivity than the other cation-exchanged samples even when the membranes are fully in proton form (i.e. they should have identical composition), as Fig. 1a shows. The model significantly over-predicts $\alpha_{0i}^{M}$ for the lithium-exchanged membranes, as Fig. 1d shows, and $\xi$ for partial cesium-exchanged membranes as Fig. 1c shows. These discrepancies may be partially attributed to the high experimental uncertainty for $\alpha_{0i}^{M}$ (calculated to be ~40% for proton-form membranes in Fig. 1d) and to lack of experimental data. Further, we assume $G$ and $\chi$ are independent of cation type, but cation-sulfonate interactions can alter the membrane microstructure causing disagreement between calculated and measured transport properties.

As the membrane exchanges from alkali cation form to proton form, conductivity increases, plotted in Fig. 1a, because protons are much more mobile than alkali cations. Figure 1b shows that the high mobility of protons causes high $\tau_{ij}^{M}$ except in membranes that are mostly exchanged with alkali cations (>50% exchanged). Equations 21 and 22 show that conductivity increases as Nafion exchanges from alkali ions to protons and $\xi$ decreases, consistent with Fig. 1c.

The high mobility of protons generates less friction for water transport through the membrane (see Eq. 6). A rising $n_{H^+/HSO_4^-}$ ratio thus increases $\alpha_{0i}^{M}$ as Fig. 1d confirms. In the absence of current, low-mobility alkali cations move down a gradient chemical potential of water as they are dragged by water, but a streaming potential develops to ensure electroneutrality and causes highly mobile water as they are dragged by water, but a streaming potential develops to ensure electroneutrality and causes highly mobile water for the different alkali cations. For these calculations, we set all other properties of A$^+$ such as a diffusion coefficient $D_{ij}^{AA}$ and where the membrane water volume fraction is $\phi_{0}$. For these calculations, we set all other properties of A$^+$ (e.g., molar viscous volume and molar mass) to those of sodium because it is in the middle of the alkali series. To provide a reference, symbols in Fig. 2 are the $D_{ij}^{AA}$ and $\phi_{0}$ at 50% cation-exchanged Nafion membranes in liquid water for lithium (triangle), sodium (square), potassium (pentagon), and cesium (diamond).

To explore these differences, Fig. 2 plots calculated transport properties for a 50% alkali ion-exchanged Nafion membrane (i.e. $n_{H^+/HSO_4^-} = 0.5$) on contour plots for (a) conductivity, (b) proton transference number, (c) electroosmotic coefficient, and (d) water, (e) ion-water, and (f) ion-ion transport coefficients as a function of $\phi_{0}$ on the y-axis and $D_{ij}^{AA}$ on the x-axis for a 50% alkali ion-exchanged Nafion membrane. Symbols plot $D_{ij}^{AA}$ and $\phi_{0}$ at 50% cation-exchanged Nafion membranes in liquid water for the different alkali cations.

Figure 2a and 2f show that $\kappa$ and $[\alpha_{ij}^{M}]$ increase with increasing cation diffusivity $D_{ij}^{AA}$ because more mobile ions have a higher flux for a given electric field or ion chemical-potential gradient, respectively. At low water contents, rising $\phi_{0}$ increases $\kappa$ and $[\alpha_{ij}^{M}]$ because larger pores and lower tortuosity facilitate increased ion transport. However, at high $\phi_{0}$, the relation is opposite because rising $\phi_{0}$ decreases ion concentrations, decreasing $\kappa$ and $[\alpha_{ij}^{M}]$.

This non-monotonic relationship between water content and ion transport causes $[\alpha_{ij}^{M}]$ of partially alkali-exchanged Nafion to follow the order Li$^+ < Na^+ < Cs^+ < K^+$, as Fig. 1f shows. Similarly, $\kappa$ has the order Li$^+ < Na^+ < Cs^+ < K^+$ because of the relationship between $\phi_{0}$ and $\kappa$ as well as because lithium and sodium...
cause stronger viscosification of the solution in the membrane (i.e. $V_{\text{Fe}} > V_{\text{Ni}} > V_{\text{Cu}}$).

Figure 2b shows the relatively small effects $\Delta_{\text{Ni}}$ and $\phi_0$ have on $t_{\text{M}}$. This explains the negligible differences in $t_{\text{H}^+}$ for different alkali ion-exchanged membranes seen in Fig. 1b. Figs. 2c–2e show that the water-transport properties, $\xi$, $\alpha_{\text{Ni}}^0$, and $\alpha_{\text{Cu}}^0$ all rise with increasing $\phi_0$. Higher water content increases pore size and decreases tortuosity, thereby increasing water transport.

The high value $\xi$ for lithium-exchanged membrane has previous been attributed to lithium “dragging” water in its large solvation shell as it transits the membrane.63,25 The effect of lithium’s large solvation and resulting high friction coefficient manifests as a relatively low $\Delta_{\text{Ni}}$ and $\phi_0$.61 This work shows that the low lithium diffusivity is not sufficient to explain the high value of $\xi$ for lithium-exchanged membranes. Rather, the large $\xi$ is due to the higher water content of the membrane and the resulting larger hydrophilic domains of these membranes. This finding is consistent with previous hydrodynamic models.77,78

The proposed model calculates transport properties of Nafion membranes exchanged with multivalent cations. Except for $\alpha_{\text{Cu}}^0$, Fig. 3 shows that the transport model (lines) is in reasonable agreement with experimental measurements64 (symbols, same transport properties as Fig. 1) for a proton-form membranes exchanged with various multivalent ions as a function of membrane proton fraction ($=n_{\text{H}^+}/n_{\text{SO}_3}$). There is relatively little difference between measured (symbols) and calculated (lines) for different alkali ion-exchanged membranes (a) conductivity $\kappa$, (b) proton transference number $t_{\text{M}}$, (c) electromosmotic coefficient $\xi$ (Fe-exchanged membrane not measured), and the transport coefficients between (d) water-water $\alpha_{\text{WW}}^0$ (Fe-exchanged membrane not measured), (e) ion-water $\alpha_{\text{iW}}^0$ (not measured), and (f) ion-ion $\alpha_{\text{ii}}^0$ (not measured) of a Nafion membrane in liquid water as a function of fractional proton exchange, $n_{\text{H}^+}/n_{\text{SO}_3}$, with calcium (right triangle), nickel (down triangle), copper (left triangle), and iron (plus sign).

Figure 4. Measured65 (circles) and calculated (solid lines) N117 conductivity as a function of external solution sulfuric acid concentration. Dashed lines denote model predictions with transport properties calculated if $\eta$ and $\phi_0$ are that of the membrane in acid-free water (i.e. $\eta = \eta(m_{\text{H}_2\text{SO}_4} = 0)$ or $\phi_0 = \phi_0(m_{\text{H}_2\text{SO}_4} = 0)$, respectively).

Dashed lines in Fig. 4 show conductivity (hypothetical) if the viscosity of the electrolyte solution in the membrane $\eta$ or the membrane volume fraction $\phi_M$ is equal to that of the membrane in acid-free liquid water (i.e. $\eta = \eta(m_{\text{H}_2\text{SO}_4} = 0)$ or $\phi_M = \phi_M(m_{\text{H}_2\text{SO}_4} = 0)$, respectively). When viscosity of the electrolyte solution in the membrane is constant, membrane conductivity does not decrease as significantly at higher acid concentrations because proton mobility would be larger. When $\phi_M$ is held constant, the conductivity increases as the acid concentration in the membrane increases. In actuality, as bulk acid concentration increases, membrane water content decreases (see Part I43) causing increased tortuosity and decreased pore size. In agreement with Tang et al.65, the delicate balance between decreasing proton mobility and increased number of charge carriers leads to a maximum in membrane conductivity at moderate acid concentrations.

Transport in concentrated electrolytes.—In concentrated electrolyte solutions, membrane water content and ion concentration induce large changes in transport properties. Part I43 shows that membrane water content decreases and acid uptake increases with increasing bulk electrolyte concentration. Figure 4 shows measured65,66 (circles) and calculated (solid line) N117 membrane conductivity as a function of external sulfuric acid concentration. Conductivity increases slightly up to a bulk electrolyte concentration of 4 mol kg$^{-1}$. At higher concentrations, conductivity decreases with increasing electrolyte concentration.

Dashed lines in Fig. 4 show conductivity (hypothetical) if the viscosity of the electrolyte solution in the membrane $\eta$ or the membrane volume fraction $\phi_M$ is equal to that of the membrane in acid-free liquid water (i.e. $\eta = \eta(m_{\text{H}_2\text{SO}_4} = 0)$ or $\phi_M = \phi_M(m_{\text{H}_2\text{SO}_4} = 0)$, respectively). When viscosity of the electrolyte solution in the membrane is constant, membrane conductivity does not decrease as significantly at higher acid concentrations because proton mobility would be larger. When $\phi_M$ is held constant, the conductivity increases as the acid concentration in the membrane increases. In actuality, as bulk acid concentration increases, membrane water content decreases (see Part I43) causing increased tortuosity and decreased pore size. In agreement with Tang et al.65, the delicate balance between decreasing proton mobility and increased number of charge carriers leads to a maximum in membrane conductivity at moderate acid concentrations.

Figure 5 plots calculated (solid line) and measured67 (symbols) membrane conductivity as a function of either vanadium III, IV or V concentration with sulfuric acid such that the total sulfate concentration is 5 mol dm$^{-3}$. The conductivity is normalized to the conductivity of the membrane in vanadium-free sulfuric acid to reduce propagation of error (see Fig. 4). Based on the proposed...
model for intermolecular friction, there is no friction between like-charged ions (see Eq. 12). Consequently, vanadium ions and protons do not directly interact at the microscopic description of the model (i.e. $\zeta^M_{ij} = 0$), but the presence of one still influences the other macroscopically (see Eq. 18). Although the current is carried mainly by protons (dotted line shows this by plotting conductivity multiplied by proton transference number, $\kappa_M^{H^+}$), as more vanadium is added to the membrane, the number of very mobile protons decreases and conductivity decreases. As Fig. 5 shows, the triply-charged $V^{III}$ displaces more protons and predicted conductivity curves are convex, whereas the singularly-charged $V(V)$ curve is concave.

In addition to conductivity and proton transference number, an array of other transport properties dictate multi-ion transport in ionomer membranes. Specifically, Figure S2 shows calculated vanadium transference numbers, electroosmotic coefficients, and $\alpha^M_{ij}$ transport coefficients of Nafion in the same electrolytes as Fig. 5. Most of the transport properties are highly concentration dependent, and are starkly different between vanadium species. Although conductivity measurements, such as those in Fig. 5, are crucial to understand transport in these membrane, this single transport property provides a limited view of the diverse processes involved in transport, a paucity of experiments can specify model parameters.

Conclusions

We develop a mathematical model for multicomponent mass transport in phase-separated cation-exchange membranes based on Stefan-Maxwell-Onsager description. Microscopic theory predicts how thermodynamic and transport properties change with ion and water concentration. The model relies on two adjusted membrane-specific parameters (Archie’s tortuosity parameter and pore-shape), whose values are physically reasonable and independent of water content and ion concentration. The model quantitatively agrees over wide ranges of electrolyte concentrations and compositions.

The proposed model shows that thermodynamic properties in Part I \(^1\) impact transport properties by controlling the concentration and identity of ions and water uptake. Membranes with less water have lower ion mobilities, mainly because the membrane tortuosity increases and the fraction that is conductive decreases. Moreover, increased ion concentration in the membrane increases the viscosity of the solution inside the hydrophilic domains of the membrane, further decreasing mobility. Consequently, the presence of mobile and fixed ions all impact transport both directly through Stefan-Maxwell-Onsager-type frictional interactions and indirectly by changing the structure of the membrane and the internal solution properties.

We fully specify the numerous transport coefficients involved in multicomponent transport by using concentrated-solution theory. The coefficients rigorously describe coupling of species transport. By building the model from physicochemical microscale description of transport, a paucity of experiments can specify model parameters. In Part III, we use the proposed theory to parameterize a model for multicomponent transport in a vanadium redox-flow-battery membrane, and demonstrate how concentrated-solution description in this system is essential to understand device performance.\(^3^0\)

Appendix A

To relate the species properties in the Experimental and Molecular Constructs, chemical equilibria of the speciation reactions give $f_{ij}$, the fraction of moles of species $i$ that partially associate into moles of species $j$.\(^3^0\)

$$s_i h_i = -\sum \limits_i s_j h_i$$  \hspace{1cm} [A1]

where the sum is over species $i$ that associate to form $j$.

The mole-weighted velocities of a fully dissociated species is the sum of the mole-weighted average velocities of its partially associated species,

$$\frac{n_i^\text{exp}}{s_i} = -\sum \limits_i \frac{n_j^\text{mol}}{s_j} \frac{v_j^\text{mol}}{s_j}$$  \hspace{1cm} [A2]

where the summation is over all species $j$ that that dissociate to $i$. Equation 8 shows that Eq. A2 relates the velocity in the two constructs via

Figure 5. Measured\(^2^7\) (symbols) and calculated (solid lines) membrane conductivity as a function of external vanadium $V^{III}$ (pentagons), $V^{IV}$ (octagons), or $V(V)$ (diamonds) concentration in sulfuric acid with a total sulfate concentration of 5 mol dm\(^{-3}\). Conductivity is normalized by the conductivity of the vanadium-free sulfuric acid solution, $n_{\text{norm}}$\(^{-0.8}\). Dashed lines are model of the proton contribution to conductivity, $\kappa_M^{H^+}$.
\[ v_i^{\text{exp}} = \sum_j f_{ij} v_j^{\text{mol}} \]  

[A3]

Taking the gradient of Eq. A1, multiplying the left side by \( c_i^{\text{mol}} / c_i^{\text{mol}} \) and the right by \( c_i^{\exp} / c_i^{\text{exp}} \) and rearranging relates the driving forces in the two constructs

\[ c_i^{\text{mol}} \nabla \mu_i = \sum_j f_{ij} (c_i^{\text{exp}} \nabla \mu_j) \]  

[A4]

where the summation is over species \( i \) that associate to form \( j \). In matrix form, Eqs. A3 and A4 are

\[ V^{\text{exp}} = FV^{\text{mol}} \]  

[A5]

and

\[ D^{\text{mol}} = gF^T (D^{\text{exp}}) \]  

[A6]

where \( F \) has elements \( F_{ij} = f_{ij} \) and is a full rank matrix with the number of columns greater than or equal to the number of rows, and the superscript \( T \) denotes the matrix transpose. Substituting the Molecular Construct form of Eq. 5 into Eq. A5 and using Eq. A6, we have

\[ V^{\text{exp}} = FV^{\text{mol}} = F[M^{\text{mol}}]^{-1} D^{\text{exp}} = F[M^{\text{mol}}]^{-1} F^T D^{\text{exp}} \]  

[A7]

where the power \(-1\) is the matrix inverse. Rearranging the Experimental Construct form of Eq. 5 and setting it equal to Eq. A7 gives

\[ [M^{\text{exp}}]^{-1} D^{\text{exp}} = F[M^{\text{mol}}]^{-1} F^T D^{\text{exp}} \]  

[A8]

Since this equality is true for any driving force on the system, \( D^{\text{exp}} \), Eq. A8 rearranges to relate friction coefficients in the Experimental and Molecular Constructs

\[ M^{\text{exp}} = (F[M^{\text{mol}}]^{-1} F^T)^{-1} \]  

[A9]

Onsager reciprocal relations holds for both \( K_i^{\text{exp}} \) and \( K_i^{\text{mol}} \) because the transformations in Eq. A9 guarantees that \( M^{\text{exp}} \) is symmetric since \( M^{\text{mol}} \) is also symmetric.

**Appendix B**

We consider a 2-D cylindrical channel with the \( z \)-direction parallel to the channel walls and the \( r \)-direction is radial. Velocity in the radial and azimuthal directions are neglected. Using the continuity equation, the steady-state equation of motion in the \( z \)-direction for a Newtonian fluid with constant viscosity and density is\(^{24}\)

\[ \frac{\partial p}{\partial z} - \sum_{i=M}^{\text{mol}} \lambda_i X_i c_i^{\text{loc}} = \frac{\eta}{r} \frac{\partial}{\partial r} \left( \frac{\partial v_z^{\text{loc}}}{\partial r} \right) \]  

[B1]

The \( r \)-velocity component is zero and where \( X_{r,z} \) is the molar external force on species \( i \) in the \( z \)-direction. The average molar body force \( X \) is equal to the mole-fraction weighted sum of molar body forces on each species, \( X = \sum X_i \lambda_i \). Radial variations of \( \eta \) are neglected, \( c_i^{\text{loc}} \) and \( v_z^{\text{loc}} \) are the local concentration of species \( i \) and fluid velocity in the \( z \)-direction, respectively, with the superscript loc denoting a function of \( r \); taking the integral average of \( v_z^{\text{loc}} \) and \( c_i^{\text{loc}} \) across the channel gives average, interstitial velocity and concentration \( v_i \) and \( c_i^{\text{mol}} \) (i.e. \( \int_0^{R_{\text{pore}}} v_z^{\text{loc}} 2\pi rdr = \frac{\pi R_{\text{pore}}^2}{4} v_i \) and \( \int_0^{R_{\text{pore}}} c_i^{\text{loc}} 2\pi rdr = \pi R_{\text{pore}} c_i^{\text{mol}} \)). Note that in this section, \( v_z \) is the interstitial velocity in a single pore. As such, \( v_z \) is isolated by \((1 - \phi_{\text{M}}) / \tau \) when appearing in Eqs. 3, 4, and 13. The Isolated Gibbs-Duhem (i.e., \( dp = \sum_{\text{mol}}^N \lambda_i (\partial n_i / \partial r) \)) equation replaces pressure changes with specific (electro)chemical potential changes

\[ \sum_{i=M}^{\text{mol}} \lambda_i \frac{\partial \mu_i}{\partial r} = \frac{\eta}{r} \frac{\partial}{\partial r} \left( \frac{\partial v_z^{\text{loc}}}{\partial r} \right) \]  

[B2]

where \( \partial \mu_i / \partial r \) includes the external force \( X_{r,z} \) (i.e. \( \mu_i \) includes potentials from external forces such as electrostatic field or gravity). Since the \( r \)-direction is in local equilibrium, \( \partial \mu_i / \partial r = 0 \). Some researchers treat electrostatic fields as an external force similar to gravity, in which case the \( \mu_i \) in the Gibbs-Duhem equation includes only the chemical potential\(^{39}\) whereas other researchers account for electrostatic interactions via an electrochemical potential, in which case \( \mu_i \) in the Gibbs-Duhem equation is an electrochemical potential\(^{40}\). Eq. B2 is the same with either approach.

We integrate Eq. B2 twice with respect to \( r \) to take the integral average to obtain \( v_z \)

\[ v_z = -\sum_{i=M}^{\text{mol}} \int_0^{R_{\text{pore}}} c_i^{\text{mol}} \frac{\partial \mu_i}{\partial r} \]  

[B3]

where

\[ \mathcal{F}_i = \int_0^{R_{\text{pore}}} c_i^{\text{loc}} \left( \frac{\partial \mu_i}{\partial r} \right) dr \]  

[B4]

and we use the boundary conditions \( \partial v_z^{\text{loc}} / \partial r (r = 0) = 0 \) and \( v_z^{\text{loc}} (r = R_{\text{pore}}) = 0 \), requiring symmetry of the fluid velocity at the channel centerline and no-slip of the velocity at the channel walls, respectively. \( \mathcal{F}_i \) is the hydrodynamic friction for a single pore and is scaled by \( \tau / (1 - \phi_{\text{M}}) \) to obtain \( \mathcal{F}_i \) in Eq. 15 that describes macroscopic of the membrane. Comparing Eqs. 15 and B4 gives \( \theta_i \)

\[ \theta_i = \frac{4G\tau}{R_{\text{pore}}^4 c_i^{\text{mol}}} \int_0^{R_{\text{pore}}} 2\pi r \left( \int_0^{r} \frac{1}{r'} \left( \int_0^{r'} \frac{c_i^{\text{loc}}}{\eta} dr'' \right) dr' \right) dr \]  

[B5]

To obtain \( c_i^{\text{loc}} \), the potential of mean force between species \( i \) and the membrane \( u_i \) dictates how \( i \) is distributed across the channel relative to its average concentration, \( c_i^{\text{exp}} / c_i^{\text{mol}} \) (i.e. radial distribution function of \( i \) with respect to \( M \)), according to\(^{39}\)

\[ c_i^{\text{mol}} \]  

[B6]

We treat the ions as fully solvated and that they cannot move past the Outer Helmholtz plane (i.e. \( u_i = \infty \) for \( r > R_{\text{effective}} \) where \( R_{\text{effective}} \) is the effective channel radius excluding the region beyond the Outer Helmholtz plane, specifically, \( R_{\text{effective}} = R_{\text{pore}} - 2R_0 \)). For the rest of the channel, we consider that the microscopic electrostatic potential \( \psi \) dictates the potential of mean force such that \( u_i = \psi_i F \) for \( r < R_{\text{effective}} \); \( \psi \) is referenced such that \( \psi = 0 \) at radial position where \( c_i^{\text{loc}} = c_i^{\text{mol}} \). With these expression for \( u_i \) and linearizing B6 for small electrostatic potentials gives\(^{56}\)

\[ c_i^{\text{mol}} = c_i^{\text{mol}} \left( 1 - \psi_i F \right) \left( \frac{RT}{H(R_{\text{effective}} - r)} \right) \]  

[B7]

where \( H(x) \) is the Heaviside step function (\( = 0 \) for \( x < 0 \) and \( = 1 \) for \( x > 0 \)). \( \psi \) is the microscopic electrostatic potential that is a function of \( r \) and \( z \) and cannot be rigorously related the macroscopic potential \( \Phi \).\(^{25}\) Poisson’s equation in cylindrical coordinates with constant relative permittivity \( \varepsilon \) dictates that for \( r < R_{\text{effective}} \) the electrostatic potential obeys\(^{56}\)
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) + \frac{\partial^2 \psi}{\partial z^2} = -\sum_{i=M}^{n_{mol}} z_{ei} F \frac{\partial \psi}{\partial z} \frac{\partial^2 \psi}{\partial z^2} = -\sum_{i=M}^{n_{mol}} z_{ei} F \frac{\partial \psi}{\partial z} + k^2 \psi
\]

where \( \varepsilon_0 \) is the permittivity of free space and the second equality uses Eq. B7 and the definition for the inverse Debye length \( k \) defined following Eq. 14. Because the macroscopic electrostatic field applied across the channel is much greater than the electrostatic field applied across the channel, \( \psi \) or \( \psi/\partial r \) is zero, and we set the second term on the right side of Eq. B8 to zero.20 Gauss’ law provides a boundary condition by dictating the total surface charge at the outer Helmholz plane equal in magnitude but opposite in sign to the excess charge density in the channel,

\[
(2\pi R_{\text{effective}}) \frac{\partial \psi}{\partial r} (r = R_{\text{effective}}) = -\sum_{i=M}^{n_{mol}} z_{ei} F \psi
\]

We find \( \psi_1 \) and \( \theta_1 \) given in Eqs. 15 and 16 using the solution for potential in Eq. B10, the distribution of ionic species in Eq. B7, and following the integration outlined in Eq. B5.

**Appendix C**

Substituting Eq. 3 into Eq. 13 and relating the mass averaged velocity to species velocities gives

\[
\sum_{i=M}^{n_{mol}} v_{i,c} \bar{w}_i = -\sum_{i=M}^{n_{mol}} \sum_{j=m} v_{f,c} (v_{j,c} - v_{i,c}) \frac{K_{ij} n_{mol} F}{\varepsilon_0}
\]

Expanding the right side of Eq. C1 and rearranging indexes gives

\[
\sum_{i=M}^{n_{mol}} v_{i,c} \bar{w}_i = \sum_{i=M,j=m} K_{ij} n_{mol} F + \sum_{i=M,j=m} K_{ij} n_{mol} F
\]

Because Eq. C2 is true for any \( v_{i,c} \), the friction coefficients must satisfy

\[
\bar{w}_i = -\sum_{j=m} K_{ji} n_{mol} F + \sum_{j=m} K_{ji} n_{mol} F + \sum_{j=m} K_{ji} n_{mol} F
\]

Solving Eq. C3 for \( K_{ij} \) and noting that \( K_{ij} = K_{ji} \) gives Eq. 14.

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