Assessing the Effects of Crowding, Pore Size, and Interactions on Electro-Osmotic Drag Coefficients

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ABSTRACT: Water flow coupled to the migration of ions is an important aspect of the performance of polymer electrolyte membrane fuel cells. The water gradients arising from the operation of fuel cells can result in flooding and drying-out of the electrodes and drying of regions of the membrane, with concomitant losses in conductivity and efficiency. The electro-osmotic drag coefficient measures the ratio between the flow of solvent molecules to that of a charged species toward an electrode in the presence of an applied electric field. The effects of variables such as pore radius, crowding, temperature, electric field strength, and ion concentration on the mobility of ions and accompanying water molecules in an applied electric field are still not well understood. Here, we investigate these factors with coarse-grained molecular simulations using an efficient model of water and sodium chloride ions and compare these results with those from previous experiments on proton exchange membranes as well as new experimental results for an anion exchange membrane. The anion exchange membranes have a smaller value of $K_{\text{drag}}$ than the proton-exchange membranes, which may be attributed to smaller water domains and a different charge carrier (hydroxide instead of protons). We directly determine the role of pore size on $K_{\text{drag}}$ and confirm that narrower pores result in less electro-osmotic drag. Our simulations show that $K_{\text{drag}}$ is sensitive to the interaction of the charge carrier with water molecules. The results of this work suggest that the most promising approach to minimize electro-osmotic drag while maintaining adequate ion conductivity is to control the morphology of the membrane structure at the microscopic level.

1. INTRODUCTION

Most fuel cell membranes are hydrated polyelectrolytes. Water flow through the membrane is an important aspect of fuel cell performance because the concentration gradients and electrode flooding that may result from excessive transport diminish the effectiveness of the fuel cell. Ions flowing toward the charged electrodes drag solvent molecules along with them. The ratio of the flux of solvent molecules to that of a particular charged species toward an electrode is known as the electro-osmotic drag coefficient, $K_{\text{drag}}$. The electro-osmotic drag coefficient can be determined in experiments by measuring the water flux across the polymer electrolyte membrane at a steady state current while maintaining the water activities at both anode and cathode at unity. Water electro-osmotic drag coefficients for various proton exchange membranes depend on temperature, water content, ion exchange polymer equivalent weight, polymer side chain structure, and identity of the ionic charge carrier. However, it is difficult to quantify experimentally to any explicit factor and its value varies depending on the experimental setup.

Pivovar et al. measured $K_{\text{drag}}$ in Nafion, polystyrene sulfonic acid, and polybenzimidazole and showed that the electro-osmotic drag coefficient depends on the identity and concentration of the electrolyte as well as the polymer structure of the membrane. They noticed that Nafion membranes had the highest conductivity but also the largest values for $K_{\text{drag}}$. The converse is true for polybenzimidazole membranes, which had the lowest conductivity and the smallest values for $K_{\text{drag}}$. They attributed the differences in conductivity and $K_{\text{drag}}$ to the varied characteristic sizes of water domains and pores in the different polymer membranes. Their results suggest that membranes with larger water domains have more bulk-like water that increases both the conductivity and the value of $K_{\text{drag}}$ relative to membranes with smaller water domains.

Ren et al. determined the values for $K_{\text{drag}}$ in poly(perfluorosulfonic acid) membranes under various operating conditions and found that $K_{\text{drag}}$ increases with temperature, in agreement with work by Ise et al. who observed an increase in $K_{\text{drag}}$ with temperature in NMR experiments. These experiments also show that $K_{\text{drag}}$ increases with increasing water content of polymer membranes. The microscopic structure of the membrane depends on its chemical building blocks and water content and has a direct impact on the charge carrier transport properties and mechanisms. As a result, the variables that affect $K_{\text{drag}}$ are interrelated and are difficult to control individually in experiments. Molecular simulations provide a...
Convenient way to separate them and investigate the impact of each individual parameter on $K_{\text{drag}}$.

Computational studies of ion-conducting membranes have primarily focused on the mobility of hydronium and water in Nafion.\textsuperscript{10–12} These studies indicate that the mobilities of protons and water are heavily influenced by the nanostructure of the membrane. The mobility of hydronium in an anion-conducting membrane has been recently studied through molecular simulations.\textsuperscript{13} There too, the water content and structure of the membrane greatly affect the transport mechanisms of ions by altering the morphology of the channels that constrain the diffusion of ions and water in the membrane. These studies of Nafion and the quaternary ammonium polysulfone hydronium membranes were performed in the absence of electric fields or any external force to induce the nonequilibrium flow of the ions.

Electro-osmotic drag coefficients have been scarcely computed using molecular simulations.\textsuperscript{9,14–17} The effects of variables such as pore radius, crowding, temperature, strength of the applied field, ion concentration, and surface roughness on the electro-osmotic mobility of water under an applied electric field are still not well understood. Thompson performed simulations of electro-osmotic and Poiseuille flow of a Lennard-Jones solvent through a 2 nm radius pore in which the electro-osmotic flow was driven by an electric field aligned with the axis of the pore.\textsuperscript{14} He determined that the flow profile conforms to continuum transport theories, except in the first monolayer of fluid near the pore wall. Aluru and co-workers compared the results of atomistic simulations and continuum theory models of electro-osmotic flow of water in nanopores and determined that continuum models are unable to capture the microscopic detail needed to describe electro-osmotic flow in pores at the nanometer scale,\textsuperscript{18–20} the most relevant range in fuel cell membranes. Molecular dynamics simulations provide a method to directly probe how changes in the microscopic scale influence the electro-osmotic drag.

Electro-osmotic drag associated with protons and hydroxide ions is of primary importance for the proton and anion exchange membranes used in fuel cells. The enhanced diffusion of protons and hydroxide ions in water in comparison to other solvated species is explained by Grotthuss hopping mechanisms whereby protons transfer between water molecules through the hydrogen bond network.\textsuperscript{21} The Grotthuss mechanism diminishes electro-osmotic drag for protons and hydroxide because it bypasses the slower vehicular transport that relies on diffusion of the solvated water molecules through the solution. Ab initio molecular dynamics simulations indicate that proton transfer events do not occur on a continuous basis, but rather there are resting periods interspersed with rapid jumps that depend on the solvation structure surrounding the hydronium or hydroxide ion.\textsuperscript{22} Simulations by Feng and Voth revealed that the proton transfer mechanism in Nafion is sensitive to the structural morphology of the proton-exchange membrane.\textsuperscript{11} The Grotthuss mechanism is favored in systems in which water is more bulk-like. Bulk-like conditions increase the electro-osmotic drag of water.\textsuperscript{23} It is still an open question what is the contribution that the Grotthuss mechanism plays in the experimental conductivity of polymer membranes. In this work, we limit our study to ions that only present vehicular transport mechanisms.

Explicit determinations of $K_{\text{drag}}$ with molecular simulations have been performed only for proton conduction.\textsuperscript{9,15–17} Choe et al. performed first-principles MD simulations that incorporated Grotthuss proton transport and measured the ratio of solvent and proton displacement using the mean-square displacement of the particles in the presence of an electric field.\textsuperscript{24} They concluded that conditions favorable to the conduction of protons via Grotthuss hopping mechanisms also increase the coefficient of electro-osmotic drag. Yan et al. performed MD simulations of perfluorosulfonate membranes to determine the velocity distributions from nonequilibrium simulations to determine drag coefficients in proton conducting membranes.\textsuperscript{16,17} These simulations did not include the Grotthuss hopping mechanism. They established that the velocity distribution of water molecules and charge carriers obeys a shifted Maxwell distribution in the direction of the applied field where the shift describes the average transport velocity. They concluded that the water molecules in the first coordination shell of the ions are the major contributors to the electro-osmotic drag by momentum transfer from the ions.\textsuperscript{17} However, it is still undetermined how labile the solvation shell surrounding the ions is under an applied force. The study of simplified systems would enable a better understanding of the underlying factors contributing to electro-osmotic drag. In this work, we use molecular simulations of model nanopores and gels to investigate the role of pore size, morphology, and temperature, as well as concentration and identity of the ions on electro-osmotic drag. We also present new experimental determinations of electro-osmotic drag in Tokuyama A201 anion exchange fuel cell membranes and compare the electro-osmotic drag to previous determinations of $K_{\text{drag}}$ in Nafion proton exchange fuel cell membranes. We interpret the experimental results in terms of the insights provided by the simulations.

The expense of fully atomistic models hinders their use for the large-scale nonequilibrium simulations necessary to quantify electro-osmotic drag. Molecular simulations with coarse-grained models provide an effective means to study effects at the microscopic level on electro-osmotic drag at a much lower computational cost. Here we model water with the monatomic water model mW\textsuperscript{23} and Na and Cl ions using the mW-Ion model.\textsuperscript{24} The water and ions in the coarse-grained model interact through short-ranged anisotropic interactions, resulting in a 100 times increase in computational efficiency compared to atomistic models. The mW water model reproduces the structure, anomalies, and phase behavior of water.\textsuperscript{21,23,25–27} The mW-Ion model reproduces the radial and angular hydration structure of the ions in solution, the equilibrium between contact and solvent-separated ion pairs, the hydration structure and dynamics of highly charged DNA polyelectrolyte, and the ratio of mobility of Cl and Na ions to water of the atomistic models across a wide concentration range, from 0.7 to 5 M salt solutions.\textsuperscript{24,28} This transferability of the model across concentrations allows us to study the effect of changing ion concentration on the electro-osmotic drag coefficient. The mW-Ion model does not have explicit charges or electrostatic interactions; therefore, we create a nonequilibrium steady-state flow by applying an external force on the ions that correspond to the one that would act on them in the presence of a homogeneous electric field. The steady-state flux of the solvent molecules with respect to the ions in solution determines the coefficient of electro-osmotic drag $K_{\text{drag}}$.

This paper is organized as follows, first we present experimental determinations of the $K_{\text{drag}}$ for proton and hydroxide-conducting polymer membranes, and then we use simulations to separately examine the effects of morphology.
and interaction strength on \( K_{\text{drag}} \). We investigate model systems, nanopores and gels, to better understand the effect of nanostructure and ion concentration on the electro-osmotic drag of water. We find that the electro-osmotic drag increases with increasing concentration of ions, increases with pore radius, and decreases under confinement. We also compute the conductivity of the model systems and find that conditions that favor ion flow also tend to increase \( K_{\text{drag}} \). Determining methods to decouple conductivity and \( K_{\text{drag}} \) is key to optimizing fuel cell membrane design. For the model systems of this work, improvements gained by minimizing the electro-osmotic drag by increasing the confinement are offset by decreases in conductivity. The trends predicted from the simulations are used to interpret experimental data for alkaline and acid fuel cell membranes. A better understanding of how the nanostructure of the membrane, the size of the ion-carrying pores, the crowding of the ions, and the tortuosity of their path, affect the transport of water and ions in membranes can help in the design of better performing ion-conducting membranes for use in fuel cell applications. Our results suggest that the most promising approach to minimize \( K_{\text{drag}} \) while maintaining adequate ion conductivity is to control the morphology of the membrane structure at the microscopic level.

2. METHODS

2.1. Simulation Methods. 2.1.A. Force Fields, Systems, and Simulation Methods. We performed molecular dynamics simulations using an efficient and accurate coarse-grained model of water, mW, as the solvent and a coarse-grained model of sodium and chloride ions that has been parametrized for use with the mW water model. This model successfully reproduces the hydration structure and the relative diffusivity of Na and Cl ions in solution as well as the experimental association constant of the Na and Cl pair in water and the association constant of the Na and Cl ions in solution as well as the experimental reproducibility of the hydration structure and the relative diffusivity of Na and Cl ions in solution as well as the experimental association constant of the Na and Cl ions in solution as well as the experimental association constant of the Na and Cl pair in water and the equilibrium between solvent-separated and contact ion pairs. A major advantage of this coarse-grained model is that it is computationally 100x more efficient than atomistic simulations, allowing for a more comprehensive study of systems and conditions than is afforded by atomistic simulations.

The coarse grained model used in this work does not include long-range electrostatics or polarizability, which may have an impact with regard to the interface interactions of the membrane walls with the ions and solution. This coarse-grained model, however, has three-body interactions that provide an environment-dependent interaction energy, an effect that can recover part of the effect introduced by polarizability in two-body potentials with electrostatic interactions.

We studied the electro-osmotic flow of water due to the drag of the ions in two types of systems: pores and “gels”. We built cylindrical pores with 4, 2, and 1 nm diameters. The 2 and 4 nm diameter pores were 6.2 nm long, and the 1 nm diameter pores were twice as long, 12.4 nm, to increase the total number of carriers and maintain the precision of the calculation. The pore walls consist of water molecules “frozen” in a configuration that corresponds to their order in a liquid solution (i.e., the equations of motion are not integrated for the molecules that make up the wall). There were 1358 particles in the wall of the 2 nm pore and 10808 in the 4 nm pore. Previous work has shown that water-wall pores are akin to MCM silica pores in terms of hydrophilicity and surface roughness. The solution inside the pore has either Na or Cl ions with a concentration of 6, 3, or 1.5 M. A number of counterions equal to the number of ions in solution in the pore are embedded into the surface of the pore wall, replacing the water particles. The average distance between the ions in embedded in the pore surface is 11, 7.7, and 5.4 Å for the 1, 2, and 4 nm diameter pores, respectively, filled with a 6 M solution. Wider pores for which all the countercharge is located at the surface would result in unphysical short distances between same-sign ions at the surface (e.g., 3.8 Å for a pore 8 nm diameter filled with 6 M solution).

In addition to the nanopores, we prepared isotropic model gels that contain ions (either Cl or Na) restrained at fixed positions while the corresponding counterions and water remain free to move. The distribution of the fixed ions (either all the Na or all the Cl in 6, 3, and 1.5 M NaCl solutions) were obtained from equilibrium configurations of bulk solutions equilibrated at 1 bar and 300 K. The fixed ions were restrained to their positions using a harmonic potential with a spring force constant of 10 kcal mol\(^{-1}\). All gel simulation cells contain a total of 8000 particles in a \( 6 \times 6 \times 6 \) nm simulation box with periodic boundary conditions in all directions. The nanopores and gel-like systems constitute zeroth order models for fuel cell membranes.

Molecular dynamics simulations were performed using LAMMPS. A force in the axial direction of the cylindrical pore and the \( x \) direction of the isotropic gels was added to the Na and Cl coarse-grained ions to replicate the effect of an applied electric field. The force applied to ions in solution is in the range of 1 kcal mol\(^{-1}\) Å\(^{-1}\), which corresponds to a field strength of \( 4.34 \times 10^8 \) V m\(^{-1}\). The external forces applied to the ions ranged from 0.1 to 2 kcal mol\(^{-1}\) Å\(^{-1}\). Unless otherwise noted, the external force applied in each simulation was 1 kcal mol\(^{-1}\) Å\(^{-1}\). These forces are comparable in magnitude to external forces used in previous simulation studies of electro-osmotic flow by Thompson (10\(^{10}\) to 10\(^{11}\) V/m),14 Yan et al. (10\(^{6}\) to 10\(^{8}\) V/m),16,17 and Choe et al. (5 \(\times\) 10\(^{8}\) V/m).15

In nonequilibrium molecular dynamics simulations, heat is dissipated into the system and it must be removed using a thermostat to maintain the steady state. The thermodynamic temperature used to thermostat the simulations is calculated by removing the center of mass velocity. Simulations were performed using the NVT ensemble and the density that corresponds to 1 bar in the absence of the force that mimics the effect of the electric field. The application of the force did not result in a significant build up of pressure in the systems. The temperature was maintained using the Nose-Hoover thermostat with damping parameter of 2.5 ps. A time step of 5 fs was used in all simulations. The nonequilibrium simulations for the pore and gel systems were evolved for 20 ns for each condition defined by system type, temperature, concentration and force on the ions.

2.1.B. Calculation of the Electro-Osmotic Drag Coefficient in Simulations. The root mean-square displacement (rmsd) was computed for both the solvent molecules and ions in solution along the three Cartesian directions. The electro-osmotic drag coefficient \( K_{\text{drag}} \) was calculated as the ratio of the flux of solvent with respect to the flux of the free ions:

\[
K_{\text{drag}} = \frac{\text{rmsd}_{\text{solvent}}}{\text{rmsd}_{\text{ion}}} \cdot \frac{\rho_{\text{solvent}}}{\rho_{\text{ion}}} \quad (1)
\]

where \( n \) is the number of free ion or solvent molecules in the simulation cell. This method of determining the electro-osmotic drag coefficient assumes that the mean-squared...
displacement in the direction of the applied force is larger than in orthogonal directions and that all free ions and water molecules contribute to the drag. The drag coefficient is normally represented as the ratio of the flux density $J$. Here, we have determined $J$ as $vC$, where $v$ is the velocity of the solvent or ion, which we calculate by $v = \text{rmsd}/t$, $t$ is time, and $C$ is the concentration. Since the water and solute share the same volume, the ratio $J_{\text{sol}}/J_{\text{an}}$ reduces to the form in eq 1 and is calculated directly from the rmsd data from the simulations.

The method described above relies on the assumption that all ions and solvent are moving, but in some circumstances, such as when the applied force is of low strength, this may not be the case if some of the ions and solvent molecules become trapped at the rough pore wall or near the immobilized counterions. To account for this possibility in the calculation of the flux, only ions and solvent molecules that move more than 1.0 Å during the 20 ns simulation are included in the calculation of $K_{\text{drag}}$. We determined this cutoff distance from the distribution of distances traveled by the ions, which shows a bimodal distribution: the ions either remained trapped vibrating within 1.0 Å of their original positions or they diffuse freely through the system.

In order to compare our results with other simulations that calculate $K_{\text{drag}}$ we verified that our method of computing $K_{\text{drag}}$ produces the same results than the methods based on distributions of molecular velocities.\textsuperscript{16,17} We compared the methods using rmsd and velocity distributions for a system with the smallest applied external field as a test case. The system comprised the 2 nm diameter pore containing 6 M NaCl in water at 300 K and 1 bar pressure. The axial force applied to the ions 1.0 kcal mol\(^{-1}\) Å\(^{-1}\). We constructed a histogram of the velocities for the Cl ions and water molecules in each Cartesian direction from a 2 ns simulation and fitted them to Maxwell–Boltzmann distributions $f(v)$:

$$f(v) = \frac{m}{\sqrt{2\pi kT}} e^{-(m(v - v_0)^2/2kT)}$$

Here, $v$ is the velocity along the axis of the applied force averaged over the simulation, $m$ is the mass of the ion or molecule, $T$ is the temperature of the system, and $k$ is Boltzmann’s constant. The shifted velocity $v_0$ represents the velocity of ions or water molecules in the axis of the applied force. The distribution of water velocities in the 2 nm pore with 6 M free Cl ions and an external field strength of 1.0 kcal mol\(^{-1}\) Å\(^{-1}\) and its fit to eq 2 is shown in Supporting Information, Figure 1. The shifted velocities $v_0$ were used to determine the fluxes of water and ions, which we employed to determine $K_{\text{drag}}$.

We found $K_{\text{drag}} = 5.5$, calculated from both the velocities and the rmsd for the same simulation. If we include only atoms that moved more than 1 Å during the simulation, the resulting $K_{\text{drag}}$ value is 4.6. This reduction is because ions and solvent molecules that are immobilized do not contribute to the flux are not included in the calculation. In what follows, we report the $K_{\text{drag}}$ values calculated using the rmsd method considering only atoms that moved more than 1 Å during the simulations.

### 2.2. Experimental Methods

#### 2.2.A. Preparation of the Membranes and Determination of the Electro-Osmotic Drag Coefficients

Nafion 117 membranes obtained from Dupont were pretreated and converted to the acid form according to the established method in literature by boiling the membrane in 3% H\textsubscript{2}O\textsubscript{2}, D.I. water, 0.5 M H\textsubscript{2}SO\textsubscript{4}, and D.I. water for 1 h each, and stored in D.I. water before use for membrane characterizations. The A201 anion exchange membrane was obtained from Tokuyama Corporation. The as-received A201 membrane primarily in the carbonate form was soaked in D.I. water for more than 1 week before use.

The membrane electrode assembly (MEA) used to measure the hydroxide anion water electro-osmotic drag coefficient across the A201 membrane was prepared by sandwiching an A201 membrane with two Pt catalyst coated electrodes in a fuel cell test hardware (Fuel Cell Technology Inc., Albuquerque, U.S.A.), which has a 5 cm\(^2\) active area. To prepare the Pt catalyst coated electrodes, a catalyst ink was formed by mixing a Pt/C catalyst (40 wt.% Pt, HiSpec 4000, Alfa Aesar) with a 50/ 50 vol % isopropanol/water solution containing AS4 anion exchange ionomer (Tokuyama) using an ultrasonic probe. The ionomer content in the dried catalyst ink was controlled at 30 wt %.

The catalyst ink was spray-coated uniformly onto a hydrophilic carbon cloth backing electrode (A-10 ELAT/NC/V2.02, hydrophilic, E-TEK) to reach a Pt/C catalyst loading of 1.0 mg cm\(^{-2}\). Both the Pt catalyst coated electrodes and the A201 membrane were pretreated by soaking in 1.0 M KOH at room temperature for 1 h, then thoroughly rinsed with D.I. water shortly before being assembled in the fuel cell test hardware. The water electro-osmotic drag tests were conducted with a hydrogen feed (50 cm\(^3\)/min at 1 atm humidified at 95 °C) at the anode for the hydrogen oxidation reaction, and with pure water feed, recirculated from a reservoir, at the cathode for the hydrogen evolution reaction, according to the experimental setup shown schematically in Supporting Information, Figure 2. The hydrogen oxidation/evolution cell was operated at a constant current mode controlled with a potentiostat (SI 1287 Electrochemical Interface, Solartron), with the cell temperature controlled by a fuel cell test station (Fuel Cell Technology Inc.) in the range of 20 to 55 °C. With the feeding hydrogen gas oversaturated for the measurement temperature, it is ensured that the water activity at both sides of the membrane remains at unit, and thus the electro-osmotic drag is the only driving force for water transport across the membrane during the measurement. At each temperature, the water loss at the cathode reservoir at zero current density was also measured. After the cell reached a stable operating condition at the selected current density, the water losses from the cathode water reservoir as a function of charge passed in 1 to 20 h were recorded to derive the water electro-osmotic drag coefficient.

For the electro-osmotic drag measurement on A201 membrane, the oversaturated hydrogen feed stream at cell anode ensures the water activity at the membrane surface remains at unit. The electrode reactions at the anode and cathode in contact with the hydroxide conducting membrane can be written as

\begin{equation}
0.5 \text{H}_2 + \text{OH}^- - K_{\text{drag}} \text{H}_2\text{O} \rightarrow (1 + K_{\text{drag}})\text{H}_2\text{O} + e^- \quad (3a)
\end{equation}

cathode:

\begin{equation}
(1 + K_{\text{drag}})\text{H}_2\text{O} + e^- \rightarrow 0.5 \text{H}_2 + \text{OH}^- - K_{\text{drag}} \text{H}_2\text{O} \quad (3b)
\end{equation}

As the result of the hydrogen oxidation and hydrogen evolution reactions, \(1 + K_{\text{drag}}\) moles of water are consumed from the cathode with every Faraday of charge past. The experimental data of the cathode water loss rates (moles of water/h) as a function of cell current density (Faraday/h) at various cell temperatures are plotted in Supporting Information, Figure 3. For each measurement temperature, the cathode...
water loss rates are proportional to the cell current density, and the value of \(1 + K_{\text{drag}}\) can be obtained from the slope of the straight line.

2.2.B. Characterization of the A201 and Naion Membranes. Membrane water-uptake: A piece of newly converted OH\(^-\) form A201 membrane was obtained by soaking in 1 M KOH for 1 h, followed by thoroughly rinsing in D.I. water. The membrane was then kept immersed in D.I. water at 60 °C for 4 h under Ar. After removing the liquid water adhering onto the membrane surface using Kimwip paper, the membrane was immediately sealed in a Ziploc plastic bag, and the wet mass \(W_{\text{wet}}\) of the membrane was recorded. By following this procedure, repeated measurements of the membrane wet mass demonstrated a low relative standard deviation at less than 2%. To obtain the dry mass \(W_{\text{dry}}\) of the membrane, the membrane was stored in a dry room with a dew point below −90 °C for over 2 days until a constant mass was reached. The membrane water uptake (WU%) was calculated according to following equation:

\[
\text{WU}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]  

The ion-exchange capacity (IEC) of A201 membrane was determined using an acid–base back-titration method. A piece of newly converted OH\(^-\) form A201 membrane was thoroughly washed with D.I. water and then soaked in a bulky volume of D.I. water for 24 h to remove any free KOH. The membrane was then reacted with a known and excessive amount of 0.1 M HCl solution for 24 h and then back-titrated with a standardized 0.1 M KOH solution using an autotitrator (Mettler Toledo T50 Titrations Excellence) equipped with a pH sensor. The measured IEC of A201 membrane at 1.68 ± 0.08 mmol/g is in agreement with the 1.7–1.8 mmol/g reported by Tokuyama.

Freshly converted OH\(^-\) form A201 membrane was used for the conductivity measurement using a four-probe cell (Bekk Tech, Loveland, U.S.A.), which was sandwiched between the two graphite cell blocks of the fuel cell testing hardware (Fuel Cell Technology Inc.) to form an airtight enclosure equipped with an inlet and outlet to provide the flow path for the conditioning gas stream over the membrane sample. A fuel cell test station (Fuel Cell Technolog Inc.) was used to control the gas flow rate and humidification temperature as well as the cell temperature for the conductivity measurements, which were carried out using a Solartron SI 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron SI 1287 Electrochemical Interface. During the measurements, an ultrapure hydrogen gas stream humidified at 80 °C ensures the membrane was in a fully hydrated state at the measurement temperature, at which the membrane was held for 30 min before commencing the conductivity measurements.

The effective equivalent conductances for H\(^+\) and OH\(^-\) in bulk aqueous solution are calculated according to Reijenga and Kenndler.\(^{33}\)

\[
\lambda = \mu I e^{-0.54^{(0.3Z^{0.48})}}
\]  

where \(I\) is the ionic strength in the membrane pores, \(Z\) is the ionic charge, and \(\mu\) is the equivalent conductance at infinite dilution.

3. RESULTS AND DISCUSSION

In what follows, we first present experimental determinations of the coefficient of electro-osmotic drag for acid and alkaline fuel cell membranes. Then, we use molecular simulations to investigate the effect of pore size and crowding on the electro-osmotic drag of Cl and Na ions in solution when all of their corresponding counterions are immobilized either on the surface of a cylindrical pore or across the volume of the mixture in the model gels. To ascertain the effect of morphology on fuel cell performance, we evaluate the evolution of ion conductivity with ion content and nanostructure for the model nanopores and gels. We also investigate how the identity of the charge carrier (Na or Cl), as well as the concentration, affect \(K_{\text{drag}}\). We discuss the experimental results in context with those of the simulations.

3.1. Acid and Alkaline Fuel Cell Membranes. Ren et al. previously measured the coefficient of electro-osmotic drag in proton-conducting membranes.\(^3\) They determined that \(K_{\text{drag}}\) increases with temperature for all membranes, and that membranes with higher water contents have higher \(K_{\text{drag}}\). They suggested that the pore structures in the membrane and the water environment in the pore are important factors influencing \(K_{\text{drag}}\). In this work, we show new experimental results of \(K_{\text{drag}}\) for the hydroxide-conducting Tokuyama membranes and compare them to the proton-conducting Naion membranes. The Tokuyama and Naion membranes have different chemical building blocks, morphologies and charge carriers, which may each modulate the electro-osmotic drag.

The number of water molecules per ion exchange site \(\lambda\) and the OH\(^-\)/H\(^+\) concentrations in the pore solutions are very similar for both A201 and Naion membranes (Table 1). For both membranes, the equivalent ionic conductivity calculated from membrane conductivity is proportional to the effective equivalent ionic conductance in solution after adjusting the effects of ionic strength. This result may indicate similar tortuous ionic conduction paths in the Naion and A201 membranes arising from hydrophilic and hydrophobic phase segregations upon membrane hydrations.

The electro-osmotic drag coefficient driven by hydroxide for the A201 membrane as a function of temperature is plotted in Figure 1, together with the water electro-osmotic drag coefficients reported in literature for the proton conducting

<table>
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<th>membrane properties</th>
<th>A201 Tokuyama membrane</th>
<th>1100 EW Naion 117 membrane</th>
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<tbody>
<tr>
<td>IEC (mEq/g)</td>
<td>1.8</td>
<td>0.91</td>
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<td>water uptake</td>
<td>68.7 wt %</td>
<td>36.4 wt %</td>
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<td>(\lambda) (H(_2)O/site)</td>
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<td>22.2</td>
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<td>mobile ion concentration in membr. (M)</td>
<td>2.77</td>
<td>2.50</td>
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<td>membr. conductivity (mS/cm) at 60 °C</td>
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<td>144.4</td>
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<td>membr. equiv conductance (S cm(^2)/eq(^{-1})) at 60 °C</td>
<td>30.1</td>
<td>57.8</td>
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<tr>
<td>eff. equiv conductance in bulk water (S cm(^2)/eq(^{-1})) at 25 °C</td>
<td>86.5</td>
<td>158.6</td>
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</table>

\(^{\text{a}}\)Calculated according to eq 5.
poly(perfluorosulfonic acid) membranes and results from the molecular simulations to be presented in the next section. The larger values of $K_{\text{drag}}$ for Nafion relative to Tokuyama A201 has also been observed by Wang et al. who measured the electro-osmotic drag in membranes equilibrated with water vapor. The distinct lower drag coefficient of the alkaline membrane leads to the question of whether it is the nanostructure of the membrane or the identity of the charge carrier that dominates the electro-osmotic drag. We note that the ratio of the conductivity in the alkaline and the acid membranes, is essentially the same as the ratio of the limiting ionic conductivities of hydroxide and proton at infinite dilution. This is possibly coincidental, as the nanostructure of the two membranes and the extent by which confinement affects the Grotthuss contribution to the transport of hydroxide and proton are not expected to be the same. Below, we use simulations to separately consider changing morphology and charge carrier to better understand the impact of these two factors. We consider two paradigmatic morphologies: nanopores with all the counterions embedded on the surface, and gels in which the counterions are uniformly spread throughout the system. The structure of real membranes may be a hybrid between nanopores and gels. We switch the identity of the pore in the positive direction. In order to determine the effect of the applied field on $K_{\text{drag}}$, we varied the strength of the force applied on each ion from 0.1 to 2 kcal mol$^{-1}$ Å$^{-1}$. In the range of forces we studied, we observed little dependence on the value of $K_{\text{drag}}$ as the force was varied (Table 2). To assess the role of pore size on electro-osmotic drag, we first calculated $K_{\text{drag}}$ for pores with diameters of 1, 2, and 4 nm and a free chloride concentration of 6 M. We found that $K_{\text{drag}}$ of water increases with the radius of the pore with values of 2.0, 4.8, and 6.9 for the 1, 2, and 4 nm pores filled with 6 M Cl, respectively. As the pore radius increased and the surface area of the pore wall relative to the solution diminished, the electro-osmotic drag increased, approaching a limiting value defined by the stoichiometric ratio of water to ions. The latter limit would imply that all water in the system was moving with the ions. These results indicate that the confinement of solutions in the microscopic pores of the membrane is an important factor influencing the magnitude of $K_{\text{drag}}$.

Of the cylindrical pores of this study, the 1 and 2 nm diameter pores are the most relevant for ion-conducting membranes, as they are comparable in size to the narrower pores connecting the water domains.

### Figure 1

Electro-osmotic drag coefficients of water in proton exchange poly(perfluorosulfonic acid) membranes (black symbols, from ref 3), A210 hydroxide anion exchange membrane (red symbols), and in the simulations of 2 nm pores (green circles), 1 nm pore at 300 K (red circle), and gels (green triangles) containing 6 M free Cl ions (and 6 M immobilized counterions) as a function of temperature, with a field strength of 1.0 kcal mol$^{-1}$ Å$^{-1}$.

### Figure 2

Profile of the simulation cell for the 2 nm radius pore (upper panel) and the gel (lower panel). The cyan balls represent the immobilized water molecules that make up the pore wall. The green balls are the chloride ions. The purple balls are the Na counterions embedded in the surface of the pore wall or immobilized in the gel. Liquid water is omitted from the images for the sake of clarity. The concentration of Na and Cl is 6 M in the two systems shown.

<table>
<thead>
<tr>
<th>Force (kcal mol$^{-1}$ Å$^{-1}$)</th>
<th>6 M</th>
<th>3 M</th>
<th>1.5 M</th>
</tr>
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<tr>
<td>2.0</td>
<td>5.1</td>
<td>10.2</td>
<td>16.5</td>
</tr>
<tr>
<td>1.0 (280 K)</td>
<td>4.6</td>
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<td>1.0 (300 K)</td>
<td>4.8</td>
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<td>16.3</td>
</tr>
<tr>
<td>1.0 (360 K)</td>
<td>4.9</td>
<td>11.5</td>
<td>16.2</td>
</tr>
<tr>
<td>0.5</td>
<td>4.8</td>
<td>11.6</td>
<td>15.4</td>
</tr>
<tr>
<td>0.25</td>
<td>4.8</td>
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<td>16.5</td>
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<tr>
<td>0.1</td>
<td>4.6</td>
<td>10.0</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Unless otherwise noted, the temperature was 300 K. The columns designed as Cl and Na represent separate simulations in which the Cl and Na ions are free in solution, respectively. The counterions are embedded on the surface of the pore wall.
in membranes such as Nafion. It is not possible to directly compare the absolute values of $K_{\text{drag}}$ from simulations of the model systems to experimental values in the membranes, but we examine the trends. Increasing the temperature results in the increase of $K_{\text{drag}}$ of water in the pores, in agreement with the experimental results for fuel cell membranes. The effect of temperature in the $K_{\text{drag}}$ of water in the pores, however, is less pronounced than for fuel cell membranes in experiments (Figure 1). This may be due to two factors. First, while the structure of the model pores of this study does not change with temperature, the porosity of fuel cell membranes has been shown to change, not always reversibly, with temperature. A second contribution to the increase in water drag with temperature dependence in proton exchange membranes arises from the increase in the ratio between vehicular to Grothuss transport mechanisms for protons and hydroxide as the temperature is increased. Only the vehicular transport mode is available to the ions of the present simulations.

To investigate how the identity of the charge carrier affects $K_{\text{drag}}$ of water, we repeated the simulations of the pores, but instead of having Cl as the free ions in solution, the Na ions were free to move and the Cl counterions were embedded in the pore wall. We found significantly larger values of $K_{\text{drag}}$ for systems with free Na ions than for systems with identical geometry containing free Cl ions (Table 2). For example, for the 2 nm pore with 6 M concentration of ions and an external field strength of 1.0 kcal mol$^{-1}$ Å$^{-1}$, $K_{\text{drag}}$ is 4.8 when the charge carrier is Cl and 10.9 when the charge carrier is Na. It may seem counterintuitive that the electro-osmotic drag of water is greater for systems in which Na is the charge carrier, because Cl ions are more diffusive than Na ions in solution and there are also more water molecules in the first solvation shell of Cl ions than Na ions.

In section 3.3 we show that the higher electro-osmotic drag for Na is associated to longer residence times of the water molecules in its first solvation shell.

The simulations indicate a pronounced decrease of $K_{\text{drag}}$ on increasing the ion concentration, in agreement with the experimental results for ion exchange membranes. An increase in concentration of chloride ions from 1.5 to 6 M in the 2 nm diameter nanopore results in the decrease of $K_{\text{drag}}$ from 10.9 to 4.8, respectively, with an applied external force of 1 kcal mol$^{-1}$ Å$^{-1}$. An increase in ion concentration is equivalent to a decrease of the water content in fuel cell membranes. However, the dimension of confinement in the membranes also changes with water content and confinement is controlled independently from the ion to water ratio in these simulations. Although early experimental determinations of $K_{\text{drag}}$ in Nafion membranes in contact with water vapor reported values essentially independent of the activity of water in the vapor, later experimental measurements in proton-conducting membranes equilibrated with water in the liquid phase determined that $K_{\text{drag}}$ increased with the water content in the membrane, as indicated by the simulations. The increase of $K_{\text{drag}}$ in fuel cell membranes on increasing water content may have two origins: the decrease in ion concentration and the modification of the nanostructure of the fuel cell membranes as the effective size of the water domains, the ion conducting phase, increases with water content. Our simulations of model nanopore systems suggest that these two factors contribute to the observed increase in $K_{\text{drag}}$.

Our study of electro-osmotic drag in nanopores shows a clear dependence of $K_{\text{drag}}$ on ion concentration and pore radius. The smaller the pore, the less water is able to accompany the ions in route to the electrode. However, unlike the nanopores studied in this work, the structure of pores in ion-conducting membranes used in fuel cells does not allow the ions an unobstructed path to the electrode. The tortuous structure of the polymer fuel cell membranes force the ions to take a more circuitous route to the electrodes. Next we discuss the effect of such disrupted structure on the electro-osmotic drag coefficient.

**3.3. Gels.** To assess the effect of crowding on $K_{\text{drag}}$ we performed constant volume and temperature simulations of “gels”: solutions of sodium and chloride ions, with one type of ions fixed to the random positions they adopt in an equilibrium configuration of the liquid solution. As the concentration of ions in the gels increases, so does the level of crowding, but the morphology of the gel remains the same (essentially a random distribution of fixed ions). The average distance between the fixed ions in the gel for the 2 and 3 M solutions, 6.5 and 8.2 Å, are comparable to the 6 to 8 Å characteristic distance between sulfonate groups in hydrated Nafion 117 membranes, while the characteristic distance for the 1.5 M gel is larger, 10.5 Å. For comparison, the average distances between ions embedded in the surface of the 2 nm pores containing 6 and 3 M solutions are 7.7 and 10.5 Å. A force was applied to the free ions along the x direction to induce the electro-osmotic flow. For each concentration, the applied force and the temperature were varied to determine the effect on $K_{\text{drag}}$.

We find that the electro-osmotic drag is smaller in the gels than in the 2 nm nanopores when the two are compared at the same ion density (Tables 2 and 3). The Cl ions must take a more circuitous route than the Na ions in the 2 nm pore with the same temperature, force, and ion concentration. Consistent with the results for the pores, we found little dependence of $K_{\text{drag}}$ in the gels on temperature within the range of this study. The confinement of the structure in the 6 M gel increases the tortuosity of the route that ions must take en route to the electrode.

$K_{\text{drag}}$ decreases as the crowding, the average distance between fixed ions in the gel, increases. The same trend is observed in Nafion membranes with a variable equivalent weight (EW): Figure 1 shows that the larger the EW, the less the water and polymer domains of the membrane are segregated, lowering the electro-osmotic drag, as shown in Figure 1. The tortuosity of the Tokuyama and Nafion membranes are similar, as discussed in section 3.1. The microscopic structure of the Tokuyama A201 membrane and, therefore, the size of domains have not

| Table 3. $K_{\text{drag}}$ Values of Water in the Gels$^a$ |
|--------------------------|-----------------|-----------------|-----------------|
| force (kcal mol$^{-1}$ Å$^{-1}$) | Cl   | Na   | Cl   | Na   |
| 2.0                       | 2.2  | 5.9  | 6.5  | 13.1 | 13.2 | 25.2 |
| 1.0 (280 K)               | 2.3  | 7.9  | 6.9  | 16.2 | 14.7 | 27.7 |
| 1.0 (300 K)               | 2.3  | 7.8  | 6.9  | 16.0 | 14.6 | 27.6 |
| 1.0 (360 K)               | 2.3  | 7.7  | 6.9  | 15.3 | 14.7 | 27.3 |
| 0.5                       | 2.3  | 8.4  | 7.2  | 17.7 | 15.2 | 29.8 |
| 0.25                      | 2.2  | 8.7  | 7.2  | 17.8 | 15.5 | 30.5 |
| 0.1                       | 1.5  | 8.8  | 7.2  | 18.5 | 15.0 | 31.1 |

$^a$Unless otherwise noted, the temperature of the simulation was 300 K.

The column designations Cl and Na represent separate simulations in which the Cl and Na ions are free in solution, respectively. The counterions are dispersed through the volume of the gel (see Figure 2) and fixed to their initial positions using a harmonic potential.
yet been reported in the literature. Nanophase segregation in Nafton is driven by the contrast between the strong hydrophobicity of the fluorinated polymer backbone and the extremely acidic sulfonate groups.12 A lower degree of nanophase segregation may be expected for the Tokuyama membrane because it is not fluorinated. Narrower water domains in the Tokuyama A201 membrane would lead to a smaller value of $K_{\text{drag}}$. This, coupled with the different Grotthuss mechanisms unique to proton and hydroxide transport, make it difficult to attribute any single characteristic to the higher $K_{\text{drag}}$ for the Nafton versus the Tokuyama A201 membrane. The complexity of real membranes underscores the utility of simplified models that individually assess the role of each contributing factor to electro-osmotic drag and also the need to model the full membranes, with their actual polyelectrolytes and hydronium or hydroxide ions, to assess the interplay of these factors in tuning the electro-osmotic drag in real membranes.

Unlike the electro-osmotic drag coefficient for NaCl where only the vehicular transport mechanism exists and the changes of drag coefficient with temperature are small, the transport of protons and hydroxide ions can also occur through Grotthuss hopping mechanisms. The relevance of Grotthuss transport in fuel cell membranes, however, is much less than in dilute solutions.22 If Grotthuss transport were to account for all the conductance, a zero drag coefficient would be expected.2 As the temperature is increased, the relative contribution of Grotthuss hopping mechanism for proton and hydroxide ion transport is expected to decrease due to a lack of favorably ordered water molecule networks required for hopping. This is reflected by the increase in the electro-osmotic drag coefficients observed for the fuel cell membranes with increasing temperature (Figure 1).

Effective fuel cell operation requires efficient mobility of the charge carrier to provide an adequate current. Ideally, fuel cell membranes should maximize ion conductivity while minimizing $K_{\text{drag}}$. We measured the velocity $v$ of ions in the direction of the field, which is proportional to the ion mobility $\mu = v/E$, where $E$ is the electric field (kept constant in the analyses that follow). We also computed the conductivity, $\sigma = c F v / E$ (where $c$ is the ion concentration and $F$ is Faraday’s constant) for the 1 and 2 nm pores and the gel with free Cl ions. The mobility of water and ions in the coarse-grained model is about 2.5 times faster than in atomistic models,24 so although the ratio of diffusivities or residence times for ions and water is well reproduced by the coarse-grained model,24,28 the actual value of the conductivity would be overestimated (by 2.5 times) in the present simulations. The higher mobility of water and ions in the coarse-grained simulations is equivalent to a scaling of the simulation time and should not affect the electro-osmotic drag coefficients.

Figure 3 plots the ionic conductivity versus the corresponding value of $K_{\text{drag}}$ for the 6, 3, and 1.5 M ion concentrations. Both the mobility of the ions and $K_{\text{drag}}$ decrease for the pore and gels with increasing ion density. Interestingly, the conductivity, which accounts not only for the mobility but also the concentration of moving ions, shows opposite trends with ion density for the pore and gels. An increase in ion density in the pores decreases the average ion mobility even though the geometry of the pore remains the same. The degree of confinement in the gel systems, on the other hand, is directly dependent on the ion density. Lower concentrations of ions in the gel result in a more open structure that allows for more unimpeded flow that increases the mobility of the ions as well as $K_{\text{drag}}$ values. To assess the role of additional obstacles in the gel system while maintaining the ion density, we performed a simulation of a 3 M NaCl gel system with an equal number of water molecules immobilized as the number of immobilized sodium ions. This 3 M gel with an additional 3 M immobilized water molecules decreases $K_{\text{drag}}$ 36% from 7.2 to 4.6 while diminishing the ion mobility 14% from 0.7 to 0.6 m/s. This suggests that controlling the morphology of the membranes to create obstacles that increase the tortuosity of flow toward the electrode but do not strongly attract charge carriers offers promise to enhance the performance of ion-conducting membranes.

Design constraints of a fuel cell membrane would determine what levels of conductivity and electro-osmotic drag are acceptable. If $K_{\text{drag}}$ was not a constraint, it would appear that maximizing the pore radius would maximize the conductivity. However, as mentioned earlier, the counterions are embedded in the pore surface and in nanopores larger than 4 nm in diameter, the charge distribution on the surface of the pore becomes unphysical. These dimensions limit the systems of interest to the 2 and 1 nm nanopores and the gels. Figure 4 shows the interplay between confinement, ionic crowding, morphology, and electro-osmotic drag. For all model systems as the water/ion ratio decreases, $K_{\text{drag}}$ decreases as well. The differences in the ion flow between the 2 nm pore and the gel systems can be attributed to the difference in the characteristic separation between immobile objects.

As with the nanopores, we performed simulations in which we switched the identity of the charge carriers, that is, the Cl ions were immobilized and the external force acted on the Na ions. Just like in the nanopore simulations, we found that the values for $K_{\text{drag}}$ were typically larger for systems with free Na ions than for systems with free Cl ions (Table 3). The number of water molecules in the solvation shell of the Cl and Na ions is 7 and 5, respectively, for 6 M solutions of NaCl in the simulations, in good agreement with experiment.24,40 Even though Cl ions have more water molecules in their solvation shell, the water molecules are pulled along more strongly by the Na ions. This results in larger values of $K_{\text{drag}}$ for systems where
the Na ion is free. This is also a trend observed in experiments of transport in ion exchange membranes in which water transference numbers for Na⁺ are lower than for Li⁺, although Na⁺ has a higher diffusion constant in solution and also more water neighbors in its first solvation shell.28

In order to better understand the difference in electro-osmotic drag coefficients between different ion species, we calculated the lifetime of water molecules in the first solvation shells of Na and Cl by constructing histograms of time lengths that water molecules continuously occupied the first solvation shell of the ions. These histograms are well represented by biexponential functions

\[ P(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \]  

The data and fit for \( P(t) \) are shown in Figure 5 for water molecules surrounding Na and Cl ions in the 6 M gel systems. The biexponential may be interpreted as arising from two distinct water ensembles characterized by short and long lifetimes represented by \( \tau_1 \) and \( \tau_2 \), respectively.41 In this work, we do not assign the lifetimes to specific water ensembles or mechanisms of relaxation. We found that the \( \tau_1 \) and \( \tau_2 \) lifetimes of water molecules surrounding the Na molecule are longer than for water molecules in the first solvation shell of Cl ions (Table 4).

Table 4 indicates that changing the strength of the applied force does not appreciably affect the lifetime of water molecules surrounding the ions. This is also represented in the values of K\(_{\text{drag}}\) having little dependence on the strength of the applied force. From these results, it is evident that the coordination shell is not long-lived enough for the electro-osmotic drag to be a result of a purely hydrodynamic type of transport mechanism where the ion carries its coordination shell in a static way toward the electrode. In fact, under the smallest applied force used in this work, 0.1 kcal mol\(^{-1}\) Å\(^{-1}\), the Cl ions in the 6 M gel move an average of 0.03 Å during the time equivalent to \( \tau_2 \), 28.4 ps. We recall that residence times in the coarse-grained model are 2.5 times shorter than in atomistic simulations.28

<table>
<thead>
<tr>
<th>( f ) (kcal mol(^{-1}) Å(^{-1}))</th>
<th>( \tau_1 ) (ps)</th>
<th>( \tau_2 ) (ps)</th>
<th>Na</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>6.6</td>
<td>28.4</td>
<td>8.7</td>
<td>66.3</td>
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<tr>
<td>0.1</td>
<td>6.6</td>
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<td>8.5</td>
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<tr>
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<td>74.5</td>
</tr>
<tr>
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<td>32.4</td>
<td>8.9</td>
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<tr>
<td>1.0 (360 K)</td>
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<td>10.7</td>
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<td>8.1</td>
<td>32.7</td>
<td>11.0</td>
<td>67.6</td>
</tr>
</tbody>
</table>

The gels in this work are a first step toward a coarse grained description of the structure of the polymer membranes and provide a more realistic representation of ion transport than the pores. However, real membranes are nonuniform and probably contain elements of both the nanopores and gels studied here. Future work will involve the development of an explicit coarse-grained representation of ion-conducting membranes.

4. CONCLUSIONS AND OUTLOOK

We used experiments and simulations to study the effects of concentration, temperature, crowding, pore size, and strength of electric field on the water electro-osmotic drag coefficient K\(_{\text{drag}}\) and the conductivity in alkaline and acid fuel cell membranes as well as in model nanopores and gels. The experiments described here represent the first study of K\(_{\text{drag}}\) in the Tokuyama A201 anion exchange membrane as a function of temperature. The simulations of K\(_{\text{drag}}\) in nanopores and gels using coarse-grained models of water and NaCl demonstrate the ability of these efficient models to provide physical insight on the factors that control the relationship between the structure of the membrane and the transport of water and ions. The coarse grained model has the reduced computational cost...
(1/100th the cost of fully atomistic simulations) needed to perform the large number of nonequilibrium simulations to measure electro-osmotic drag. This allowed the exploration of a wide range of conditions that would not have been accessible otherwise.

Our simulations indicate that narrowing the pore size results in a diminishing value of the electro-osmotic drag coefficient. Pivovar et al. and Ren et al. observed greatly different values of $K_{\text{drag}}$ in various polymer membranes and suggested that the size of the water domains in the membrane strongly influences the magnitude of $K_{\text{drag}}$. Here we have directly determined the role of pore size on $K_{\text{drag}}$ and confirmed their inference that narrower pores result in less electro-osmotic drag. To better understand the electro-osmotic drag in ion-conducting membranes, we constructed model gels made of immobilized counterions that represent a zeroth order representation of fuel cell polymer membranes. The confining geometry of the gels reduces the amount of bulk-like water while simultaneously increasing the tortuosity of the paths that the ions must take, resulting in reduced $K_{\text{drag}}$ for the gels with respect to nanopores with the same ion density. Changes in the strength of the applied field do not appreciably affect $K_{\text{drag}}$.

$K_{\text{drag}}$ is sensitive to ion–water interactions. Free Na ions have larger $K_{\text{drag}}$ than free Cl ions. Lifetime of water molecules in the first coordination shell of Na ions is longer than that of water molecules in the first coordination shell of Cl ions. Therefore, a portion of the contribution of $K_{\text{drag}}$ is unique to the identity of the charge carrier, and attempts to reduce $K_{\text{drag}}$ should focus on other contributing factors that can be systematically controlled.

These results suggest that controlling the morphology and structure of the membrane would provide the greatest promise in minimizing the effect of $K_{\text{drag}}$ while maintaining ion conduction. Tokuyama anion exchange membranes have smaller $K_{\text{drag}}$ than Nafion proton exchange membranes. It remains an open question on how much of the reduced $K_{\text{drag}}$ in the anion exchange membrane is due to the differences in dimensions of segregation between the polymer membranes or the different Grothhuss hopping mechanisms involved in proton and hydroxide conduction. Further studies are needed to characterize the microscopic structure of alkaline membranes in experiments and simulations.

The insights gained from this model can inform studies to measure electro-osmotic drag coefficients in fully atomistic simulations that may be performed in the future. Molecular simulations provide a powerful tool to explain the effect of many contributing factors affecting electro-osmotic drag. Modeling of fuel cell membranes would provide predictive data useful for the optimization of their performance. Molecular simulations that account for the specific chemical structure of the membranes and the proton or hydroxide charge carriers would be useful in establishing the explicit factors that influence electro-osmotic drag.

Fuel cell membranes are heterogeneous in length-scales that are challenging to access with molecular models, even the efficient coarse-grained models of this study. An avenue to address this would be the integration of the results of this study for simplified structural membrane elements into multiscale models that can capture the behavior at larger scales. A multiscale, multiresolution modeling approach would be useful to elucidate the effect of connectivity of water domains on the molecular transport of fuel cell membranes. The integration of molecular and finite element levels of modeling would contribute to the realization of a “materials by design” strategy to improve the performance of fuel cell materials.

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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