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Thermodynamics and Proton Transport in Nafion - III. Proton Transport in Nafion/Sulfated ZrO(2) Nanocomposite Membranes

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A proton transport model is proposed to describe proton diffusion in Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membranes. The model considers the water content which could be determined by thermodynamics, dissociation of protons near the acid surface, stabilization of protons in water, and the strength and concentration of acid sites from Nafion as well as ZrO\(_2/\text{SO}_4^{2-}\). The transport of proton occurs via a sluggish hopping process through the membrane surface, and relatively fast structural and ordinary mass diffusion of hydronium ions in the bulk of the membrane pores. The conductivity of the in situ sol-gel prepared Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membranes is accurately predicted as a function of relative humidity without any fitted parameters. Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membrane shows higher proton conductivity compared with Nafion at the same temperature and humidity conditions due to the improved water uptake and provision of strong acid sites. The model provides a theoretical framework for understanding proton conduction in nanocomposite membranes and can be successfully used to develop high-conducting membranes for fuel cell applications.

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Experimental

Membrane preparation.—A Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membrane was prepared via in situ sol-gel technique and compared with unmodified Nafion in terms of water uptake and proton conductivity for different relative humidity conditions. The objective of this paper is to understand the proton-transport mechanism in nanocomposite membranes so that the favorable properties of inorganics for high proton conductivity can be derived to design new membranes for fuel cells. A theoretical proton conductivity model is developed based on the parallel pore model incorporating various proton-transport mechanisms such as surface proton hopping, Grotthuss diffusion, and traditional in masse diffusion.
Water uptake and proton conductivity measurements.—The experimental details of water uptake and proton conductivity are provided previously.22,23

Theory

Figure 1 shows a schematic representation of the nanocomposite membrane. The absorbed water molecules interact with the host membrane as well as the incorporated inorganics. The water molecules within the nanocomposite membrane can be classified as “bulk water” away from the acid groups and “surface water” near the acid groups. Thus, it is assumed that the protons in the nanocomposite membranes diffuse via (i) a surface diffusion mechanism close to the acid groups or under low water activity, and (ii) a bulk diffusion mechanism in the region away from the acid groups or under high water activity condition. In the bulk, proton diffusion is predominantly via the Grotthuss mechanism, but the $\text{H}_3\text{O}^+$ ion also undergoes traditional mass diffusion, i.e., the so-called en masse diffusion. The overall proton conductivity of nanocomposite membranes $\sigma_{\text{H}^+}$ can be written as:

$$\sigma_{\text{H}^+} = \frac{e}{\tau} \left[ \frac{F^2}{RT} \left( D_{\text{H}^+}^0 C_{\text{H}^+}^0 + D_{\text{H}^+}^\text{G} + D_{\text{H}^+}^l \right) \right]$$

where $e_i$ is porosity of membrane, $\tau$ is tortuosity factor, $F$ is Faraday’s constant, $R$ is the gas constant, $T$ is temperature, $D_{\text{H}^+}^0$, $D_{\text{H}^+}^\text{G}$, and $D_{\text{H}^+}^l$ are the diffusion coefficients for the surface, Grotthuss, and en masse mechanisms, respectively, and $C_{\text{H}^+}^0$ and $C_{\text{H}^+}^\text{G}$ are the concentrations of protons participating in the bulk and surface phases, respectively.

Parameter Identification

Diffusion coefficients.—The acid groups of nanocomposite membrane are composed of those of the host membrane (i.e., Nafion) and solid acid (i.e., ZrO$_2$/SO$_4^{2-}$). The surface diffusion coefficient of protons can be obtained from

$$\frac{1}{D_{\text{H}^+}^0} = \frac{x_M^x}{D_{\text{H}^+}^M} + \frac{x_{\text{SA}}^x}{D_{\text{H}^+}^\text{SA}}$$

where $D_{\text{H}^+}^M$ is the diffusion coefficient of proton via the acid group of the host membrane (M), $D_{\text{H}^+}^\text{SA}$ is the diffusion coefficient of proton via the acid group of the solid acid (SA), $x_M^x$ is the fraction of proton attached to the host membrane, and $x_{\text{SA}}^x$ is the fraction of proton attached to the acid groups of the solid acids. The fraction of membrane acid groups can be written in terms of the molar ratio of solid acid and membrane acid group, or $x_M^x = 1/(1 + q)$ and $x_{\text{SA}}^x = q/(1 + q)$, where $q$ = moles of acid sites from (ZrO$_2$/SO$_4^{2-}$)/mole of SO$_4$. For $w$ grams of solid acid with the average particle of diameter $d_w$, the moles of effective surface acid from the solid acids is $(6w/d_w \rho \theta) C_{\text{H}^+,\text{SA}}^*$, where $\theta$ is particle density, and $C_{\text{H}^+,\text{SA}}^*$ is the effective surface site density of acid groups from the sulfated zirconia. Thus, the molar ratio of acid site for $w$ grams of solid acid per gram of host membrane can be written as

$$q = \frac{6w}{d_w \rho \theta} E_W C_{\text{H}^+,\text{SA}}^*$$

where $E_W$ represents the equivalent weight of the host membrane.

The surface diffusion coefficients, $D_{\text{H}^+}^M$ and $D_{\text{H}^+}^\text{SA}$, can be obtained by applying the Einstein-Smoluchowski relation:

$$D = \frac{k_B T}{6 \pi \eta d_w}$$

where $k_B$ is the mean step distance, $\kappa$ is the dimensionality constant, and $\tau = 1/\nu_0$ is the mean time between successive steps. The hopping time is provided by $\nu_0 = k_B T/h$ in which $k_B$ is the Boltzmann constant and $h$ is the Planck constant, and $\Delta G_{\text{e}0}$ is the effective Gibbs free energy of activation for surface diffusion around the acid groups. Substitution of the acid fractions (i.e., $x_M^x$ and $x_{\text{SA}}^x$) and diffusion coefficients (i.e., $D_{\text{H}^+}^M$ and $D_{\text{H}^+}^\text{SA}$) into Eq. 2 gives

$$\Delta G_{\text{e}0} = \frac{q \nu_0}{4 \pi \eta d_w} \left[ \frac{1}{R_i + R_f + l} \right]$$

where the number 4 in the denominator originates from the dimensionality constant for 2D surface diffusion, $\Delta G_{\text{e}0}^0$ is the effective Gibbs free energy of activation for the surface diffusion around membrane acid groups, and $\Delta G_{\text{e}0}^\text{SA}$ is the effective Gibbs free energy of activation for the surface diffusion around acid groups of the solid acid. The Gibbs free energy $\Delta G_{\text{e}0}^\text{SA}$ can be calculated by assuming that the first step is rate-determining for the overall surface proton hopping based on the quick decreases in coulombic interaction energy with the distance from the acid sites and low dielectric constant of water in the surface layer:

$$\Delta G_{\text{e}0}^\text{SA} = \frac{(q_e)^2}{4 \pi \varepsilon_0 \varepsilon_r} \left[ \frac{1}{R_i + R_f + l} \right]$$

where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the medium, $q_e$ is the electrostatic charge, $R_i$ is the effective radius of acid groups, and $R_f$ is the radius of the hydronium ion.

The diffusion coefficient for the Grotthuss mechanism depends on the rate at which the hydrogen bond forms and breaks between proton donating and receiving water molecules. The proton in aqueous solution is commonly visualized as hydronium ion H$_3$O$^+$ in which three hydrogen atoms share the charges equally, or Zundal ion H$_2$O$^+$ in which a proton is shared between two water molecules, or
Eigen ion $\text{H}_3\text{O}^+$ in which hydronium ion is strongly bound with three water molecules. In fact, there are many and complex states of hydrated protons $\text{H}^+\text{(H}_2\text{O})_n$, and the three states are considered only as limit or ideal structures. The rate-determining step for proton transport includes hydrogen-bond cleavage between the proton-accepting water molecule and a nearby water molecule, and reorientation of the proton-accepting molecule toward the hydronium ion to be in a receptive position. The rotational diffusion coefficient of the water molecule can be written as:

$$D_R = k_B T / 8 \pi \eta R_w^3$$

[6]

where $\eta$ is the viscosity of water and $R_w$ is the radius of water molecule. Using the Einstein relation $\tau_D = 1 / 2D_R$, the relaxation time is given as

$$\tau_D = 4 \pi \eta R_w^3 / k_B T$$

[7]

It has been suggested that the microscopic water reorientation time is some fraction of the relaxation time (e.g., $2\pi \eta / 3$). The proton diffusion by the Grotthuss mechanism is characterized by the water reorientation time $\tau_D = 1.5$ ps at room temperature, which is measured and also calculated from the relation between the force of water dipole with the hydronium ion and torque for translational rotation. Thus, the Grotthuss diffusion coefficient is calculated as $D_G^H = 7 \times 10^{-5}$ cm$^2$/s from $D_G^H = 1 / 6 \nu / \eta$, where $l_Q = 0.255$ nm, O-O distance of $\text{H}_2\text{O}_2^+$ ion, and $\tau_D = 1.5$ ps.

The en masse diffusion coefficient of hydronium ion in the medium consisting of water, membrane acid site, and solid acids can be written as

$$\frac{1}{D_{H^+}^E} = \frac{x_w}{D_{H^+}^w} \left( 1 + \frac{x_M D_{H^+}^M}{x_w D_{H^+}^w} + \frac{x_{SA} D_{H^+}^SA}{x_w D_{H^+}^w} \right)$$

[8]

where $x_w$, $x_M$, and $x_{SA}$ denote the fraction of water, membrane, and solid acid, respectively, and $D_{H^+}^w$, $D_{H^+}^M$, and $D_{H^+}^SA$ denote the Stefan-Maxwell diffusion coefficients of hydronium ion and bulk water, hydronium ion and polymer matrix, and hydronium ion and solid acids, respectively. It is assumed that the effective surface molecules of solid acid serve as molecular particles for the en masse diffusion. The fraction of water in the membrane can be written as $x_w = \lambda_w / (\lambda_w + 1)$, where the solvent loading $\lambda_w$ is given by

$$\lambda_w = \frac{p (1 + w)}{MW_w \left( 1 + \frac{6w}{d_{H^+}^w} \right) C_{H^+,SA}^e}$$

[9]

where $p$ is the mass of absorbed solvent per mass of dry noncomposite membrane and $MW_w$ is the molecular weight of water. Using the analogy between the Einstein-Smoluchowski relation and elementary kinetic theory, the diffusion coefficient ratios can be calculated as:

$$\frac{D_{H^+}^w}{D_{H^+}^M} = \frac{\sqrt{2}}{2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2} \text{ and } \frac{D_{H^+}^w}{D_{H^+}^{SAw}} = \frac{\sqrt{2}}{2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2},$$

where $\tau_{SMw}$ and $\tau_{SMw}$ are the ratios of partial molar volume of membrane to that of water, and partial molar volume of solid acid to that of water, respectively. Applying these into Eq. 8 and from $x_M / x_w = \lambda_w (1 + g)$ and $x_{SA} / x_w = g / \lambda_w (1 + g)$, the en masse diffusion coefficient of hydronium ion for the medium composed of water, polymer matrix, and solid acids can be written as

$$D_{H^+}^E = \left\{ \begin{array}{ll} \lambda_w (1 + \frac{6w}{d_{H^+}^w} E_{W,M} C_{H^+,SA}^e) & \text{if } \lambda_w (1 + \frac{6w}{d_{H^+}^w} E_{W,M} C_{H^+,SA}^e) \geq \sqrt{2} (\tau_{SMw})^{3/2} + \sqrt{2} (\tau_{SMw})^{3/2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2} \\
\lambda_w (1 + \frac{6w}{d_{H^+}^w} E_{W,M} C_{H^+,SA}^e) + \sqrt{2} (\tau_{SMw})^{3/2} + \sqrt{2} (\tau_{SMw})^{3/2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2} \left( \frac{\tau_{SMw}}{\tau_{SMw}} \right)^{3/2} & \text{otherwise} \end{array} \right\} D_{H^+}^w$$

[10]

Thus, the en masse diffusion coefficient depends on the amount of water uptake ($\lambda_w$), particle size of inorganics ($d_p$), the amount of loading of inorganics ($w$), the ratio of partial molar volume of host membrane to water ($r_{M/w}$), the ratio of partial molar volume of inorganics to water ($r_{SA/w}$), surface acid site density of the inorganics $C_{H^+,SA}^e$, and the hydronium ion diffusion coefficient in aqueous water ($D_{H^+}^w$).

The diffusion coefficient of hydronium ion through water $D_{H^+}^w$ is obtained from the Stokes-Einstein relation or usually approximated as the self-diffusion coefficient of water, which has been reported as $2.1-2.3 \times 10^{-5}$ cm$^2$/s at room temperature. Considering hydronium ion as a diffusing entity in the medium of water, the Stokes-Einstein relation provides

$$D_{H^+}^E = \frac{k_B T}{6 \pi \eta R_w^3}$$

[11]

where $\eta$ is the viscosity of the medium and $R_{H^+,O}$ is the hydrodynamic radius of hydronium ion. Because the Stokes-Einstein equation provides an approximation of the diffusion coefficient for molecular species and the concept of hydrodynamic radius is rather unclear, we take $D_{H^+}^w$ as the self-diffusion coefficient of water. In fact, this corresponds the effective water radius $R_{H^+,O} = 0.108$ nm, smaller than the geometric radius of water molecule $R_{H^+,O} = 0.143$ nm. Because the experimental diffusion coefficient of proton in water is known as $9.31 \times 10^{-5}$ cm$^2$/s at room temperature, the Grotthuss diffusion coefficient can also be obtained by subtracting the self-diffusion coefficient of water from the experimental proton diffusion coefficient.

Distribution of protons between the surface and bulk regions.—Some of the dissociated protons remain close to the anion surface sites and participate in surface diffusion, whereas others with a higher degree of hydration break away into the pore bulk and participate in bulk diffusion comprised of Grotthuss and en masse mechanisms. Here we assume that dissociated acid sites with up to two water molecules remain close to the surface to the pore bulk. The total concentration of acid sites is calculated as $C_{H^+,i} = 1 / \lambda_w \bar{V}_w$, where $\bar{V}_w$ is partial molar volume of water, and the concentration of surface protons $C_{H^+,i}^e = C_{H^+,i} \theta_1 + \theta_2$, where $\theta_1$ denotes the fraction of acid sites with $i$ bound water molecules. Because the acid sites are in the host membrane and solid acids, the total surface concentration is $C_{H^+,M} = \sum_{i=1} C_{H^+,i}^e$. In terms of surface fraction of total concentration, the surface concentration can be written as $C_{H^+,M} = f_{SA} C_{H^+,SA}$ and $C_{H^+,SA} = f_{SA} C_{H^+,SA}$, where $f_{SA}$ represents the surface fraction of protons near the host membrane and solid acid, respectively.
where \( v \) is the number of equilibrium steps with acid groups, \( K_i \) is equilibrium constant between water and acid groups, and \( a_w \) is the activity of water in surroundings. The bulk concentration of proton is given by \( C_{H^+} = C_{H^+,0}(1 - \theta_0 - \theta_1 - \theta_2) \) and can be approximated as \( C_{H^+} = C_{H^+,0} - \sum C_{H^+,M} \). Because the dissociation constants in water \( K_1 \) and \( K_2 \) may be different for sulfonyl acid and solid acids, the concentrations of surface proton also vary with the strength of ions. The equilibrium constants \( K_{1,M} \) and \( K_{2,M} \) are taken as 1000 and 200, respectively, based on the dissociation constant of sulfonylic acid and the proton affinity data.\(^{33,35}\)

The sulfated zirconia is usually regarded as\(^{36}\) "superacid" (\( H_0 < -16 \)) due to its strong acidity, which is greater than that of 100% sulfuric acid in which the activity of water in surroundings. The bulk concentration increases monotonically with water content.

Porosity and tortuosity.—The total volume of the nanocomposite membrane is the sum of the three components, water, host membrane, and solid acid. The porosity of the membrane can be obtained from\(^{37}\)

\[
e_i = \frac{\lambda_w(1/EW_M + w/MW_{SA})}{\lambda_w(1/EW_M + w/MW_{SA}) + \tau_{SA}/EW_M + w_{SA}/MW_{SA}}
\]

The tortuosity factor \( \tau \) is usually determined experimentally. Here, we use Preger’s model\(^{37}\) in which the tortuosity factor \( \tau \) depends on the porosity \( e_i \), which in turn varies with the amount of water uptake, equivalent weight of host membrane, the amount of inorganics, molecular weight of inorganics, and the ratios of partial molar volumes as shown in Eq. 14.

Results and Discussion

Table I shows the water sorption data of Nafion and Nafion/\((\text{ZrO}_2/\text{SO}_4^{2−})\) nanocomposite membranes at 25 and 90°C. The incorporation of \(\text{ZrO}_2/\text{SO}_4^{2−}\) increases water uptake as well as provides new acid sites for proton transport. The structure of \(\text{ZrO}_2/\text{SO}_4^{2−}\) has been studied extensively and many surface models have been proposed.\(^{30-42}\) Figure 2 shows the interconversion of Lewis acid site into Bronsted acid sites by the presence of water molecules, which was observed by IR spectra of pyridine adsorption.\(^{33}\) The total acid site of the nanocomposite membrane is the sum of acid sites, \( C_{H^+,SA} = C_{H^+,SA(B)} + C_{H^+,SA(L)} \), where \( C_{H^+,SA} \), \( C_{H^+,SA(B)} \), and \( C_{H^+,SA(L)} \) denote the concentration of the total, Bronsted, and Lewis acid sites, respectively. The surface site density is reported\(^{44}\) in a range of \(10^{16} \) to \(10^{18}\) molecules/m\(^2\), and \( C_{H^+,SA} = 10^{10} \) molecules/m\(^2\) is taken, which corresponds to \(1.67 \times 10^{15}\) mol/mol. It is assumed that both sites are responsible for the generation of hydronium ions and participate in the transport of protons in the nanocomposite membrane. Table II shows all the parameters for estimating diffusion coefficients in the nanocomposite membranes. The amount of \(\text{ZrO}_2/\text{SO}_4^{2−}\) added to the host membrane was determined as 3 wt % by ash analysis. Figure 3 shows the surface diffusion coefficient of nanocomposite membrane as a function of acid site density. As the acid site density increases, the surface diffusion coefficient increases with the density of acid sites provided by \(\text{ZrO}_2/\text{SO}_4^{2−}\). The acid site density is directly related to the size of particle by Eq. 3; that is, the increase in site density \( C_{H^+,SA} \) has the same effect in the decrease in the particle size \( d_p \). Therefore, the small size with high surface acid density is favorable for high surface diffusion of protons in the nanocomposite membrane. The surface diffusion coefficient of Nafion is \(1.01 \times 10^{-7}\) cm\(^2\)/s at 25°C, which is obtained by substituting \( w = 0 \) in Eq. 4. Figure 4 shows the en masse diffusion coefficients of nanocomposite membrane at 25 and 90°C. The diffusion coefficient increases with the vapor phase activity due to the increase of water content as shown in Eq. 10. The model predicts the diffusion coefficients of \(1.35 \times 10^{-7}\) cm\(^2\)/s at 25 and 90°C, respectively, for the nanocomposite membrane contacting with saturated water vapor. This is about two orders of magnitude higher than the surface diffusion coefficients at the same temperature and activity conditions. In general, the surface diffusion process is considerably slower than the bulk process because of the strong coulombic interaction around the surface acid sites.\(^{35,46}\) The coulombic barrier plays a central role in the surface diffusion and causes high activation energy for the transport of protons, while the bulk diffusion pro-

![Figure 2. Structure of ZrO₂/SO₄²⁻ solid acid.](image)
cesses are of relatively low energy barriers. Figure 5 shows the experimental conductivity data of Nafion along with the model at 25 and 90°C, respectively. The Grotthuss diffusion coefficient can be calculated\textsuperscript{47-49} by subtracting the en masse diffusion coefficient which is approximated by the self-diffusion coefficient of water molecule for the temperature range 0-100°C\textsuperscript{50} from the total diffusion coefficient, which is obtained from the limiting ionic molar conductivity data given by 51

\[
\frac{\mathcal{D}_{H^+}}{\mathcal{D}_{H^+},T} = \frac{\mathcal{D}_{H^+},25C}{\mathcal{D}_{H^+},0} = 1 + 0.0139(T - 25^\circ C),
\]

where \(\mathcal{D}_{H^+},25C\) and \(\mathcal{D}_{H^+},T\) are the limiting molar conductivity of proton at 25°C and temperature \(T\) °C. It is noteworthy that the use of concentration-independent diffusion coefficients in Eq. 1 is valid only for strong acid and low molar concentrations where the concentration-dependent coefficient \(\chi\) is negligible in Kohlrausch’s law \(\lambda = \lambda_{0} - \chi \cdot C\), where \(\lambda\) is molar conductivity, \(\lambda_{0}\) is limiting molar conductivity, and \(C\) is molar concentration of an ion.\textsuperscript{24,52} The model predicts proton conductivity of Nafion to be 0.04 and 0.08 S/cm at 25 and 90°C for 80% relative humidity conditions, respectively. Figure 6 shows the proton conductivity of Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membranes. The proton conductivity of nanocomposite membrane is higher than that of Nafion over the whole activity range of water vapor. For example, at 80% relative humidity, the conductivities of 0.06 and 0.105 S/cm are predicted at 25 and 90°C, respectively. This is due to the increased water uptake along with the provisions of strong acid sites by \(\text{ZrO}_2/\text{SO}_4^{2-}\). Figure 7 shows the effect of temperature on the proton conductivity at 80% relative humidity condition. Nafion/\(\text{ZrO}_2/\text{SO}_4^{2-}\) nanocomposite membranes show higher proton conductivity than unmodified Nafion for all the range of temperature. The proton conductivity of Nafion can be improved by 20% with the incorporation of \(\text{ZrO}_2/\text{SO}_4^{2-}\) in the host membrane if the model parameters such as particle size and particle distributions are carefully controlled during the preparation procedure. The analytical model suggests that the polymer/inorganic nanocomposite membranes can provide better proton conductivity than unmodified membranes. Further, the nanocomposite membranes are expected to enhance thermal and mechanical stability of the polymer membrane at high temperature.\textsuperscript{53}

### Table II. Parameter values employed in the model at room temperature.

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<th>Diff. coeff.</th>
<th>Symbols</th>
<th>Values</th>
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<th>Comments</th>
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<td>(D_{H^+})</td>
<td>EW(\text{M})</td>
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**Figure 3.** The effect of acid site density on the surface diffusion coefficient.

**Figure 4.** The effect of water vapor activity on the en masse diffusion coefficient.
Conclusions

A comprehensive proton transport model in Nafion/(ZrO2/SO42-) nanocomposite membrane has been proposed based on the understanding of structural and physicochemical properties of the membranes. The solvent (i.e., water) sorption, the dissociation of protons around the acid sites, and the distribution of protons in the hydrated Nafion/(ZrO2/SO42-) nanocomposites have been taken into consideration prior to the diffusion process. The transport model distinguishes the surface and bulk mechanisms of proton transport in the nanocomposite membrane in which the proton conduction depends on the water content, diffusion coefficients at the surface and bulk regions in the membrane, and concentration and distribution of protons. The surface diffusion of proton, which takes place dominantly under low-humidity environments, is slow due to high coulombic interaction around the acid surface, while the transport of protons in the bulk water is relatively fast and occurs via Grotthuss and en masse mechanisms. The sol-gel incorporation of ZrO2/SO42- into Nafion increased the amount of water uptake and provided additional acid sites for proton diffusion, which resulted in higher proton conductivity compared to the host membrane. The results are encouraging and the polymer/inorganic membranes can be classified as a promising family of PEMs for fuel cells. The transport model developed here offers a theoretical framework for understanding the proton transfer in nanocomposite membranes and should also be helpful in systematically developing high proton-conducting nanocomposite membranes based on the incorporation of inorganic materials into the host membranes.

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