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Thermodynamics and Proton Transport in Nafion

II. Proton Diffusion Mechanisms and Conductivity

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A comprehensive pore transport model is proposed to describe proton diffusion within Nafion at various hydration levels by incorporating effects of water uptake and various proton transport mechanisms, namely, proton hopping along surface, Grotthuss diffusion, and ordinary mass diffusion of hydronium ions. The diffusion coefficients are predicted within a general random walk framework. The proton conductivity in contact with water vapor is accurately predicted as a function of relative humidity without any fitted parameters, considering the sorption isotherm proposed in the companion paper (Part I). A maximum conductivity in contact with liquid water is also predicted by the model for equivalent weight between 900 and 1000, in good agreement with the experimental measurements. The modeling framework could be extended to other proton conducting electrolytes for fuel cell applications.

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The proton exchange membrane (PEM) plays a central role as a medium for proton conduction in PEM fuel cells. Due to the importance of proton transport on fuel cell performance, studies on the proton transport have been conducted not only for understanding the transport mechanism but also for help in designing alternate PEMs based on a fundamental appreciation. Nafion, the most attractive polymer electrolyte developed so far, shows excellent proton conductivity, but only when soaked in water, which is the medium for proton transport.^{1,2} In a companion paper (Part I),³ we have provided a thermodynamic model for the sorption of water in PEM. Here, we consider the related problem of proton diffusion in hydrated PEMs.

The study of proton transport in aqueous solution has received considerable attention for over a century because of its paramount importance in chemical, biological, and electrochemical systems. In aqueous solutions of acids, the proton exists as hydronium ion, which is itself hydrated, *e.g.*, as H_5O_2^+ or H_9O_4^+ .^{4,5} The mobility of the proton is abnormally high as compared with other ions of a size similar to hydronium ion, and is explained in terms of contribution by the so-called Grotthuss mechanism, or the “relay” mechanism, in which the transport of protons is determined by the rate at which the hydrogen bond between a hydronium ion and a water molecule forms rather than by the slower rate at which hydronium ions may migrate *en masse*, also called the vehicular mechanism. The Grotthuss mechanism was proposed about two hundred years ago,⁶ and later further developed by Huckel,⁷ Bernal and Fowler,⁸ Conway *et al.*,⁹ and Agmon.¹⁰ More recently, a number of molecular dynamic (MD) simulations have been proposed to model the transport properties of an excess proton in bulk phase water.¹¹⁻¹⁶

The transport of protons in PEMs is strongly dependent upon the structure and physicochemical nature of the polymer with the level of hydration. Despite substantial efforts to understand proton transport phenomena in PEMs based on statistical mechanics,¹⁷ phenomenological approaches,^{18,19} and MD simulations,²⁰⁻²⁴ a comprehensive transport mechanism in PEMs has not yet been advanced due to their complex nanostructure and inhomogeneous nature when hydrated.

In this paper, we present a conductivity model that provides a comprehensive phenomenological picture of proton transfer in Nafion. The model is based on the parallel pore structural model and incorporates the various proton transport mechanisms such as surface proton hopping, Grotthuss diffusion, and the traditional *en masse* diffusion, including the frictional interactions with the mem-

brane. The analysis here provides a theoretical framework for the general understanding of the proton transport in PEMs.

Experimental

Proton conductivity measurements.—The preparation procedure of Nafion membranes is described in Part I.³ A Nafion sample was sandwiched between two Pt electrodes, each on either side of the membrane to measure the conductivity, and placed in a humidity-controlled chamber. The humidity of the chamber was monitored utilizing a dew point/temperature probe (HMP 238, Vaisala, Woburn, MA). A dry nitrogen stream was saturated with water by passing it through a humidifier, which was then combined with a dry stream of nitrogen to control the relative humidity (RH). The conductivity was measured at 25°C from 0 to 99% RH. Measurements were made with a perturbation voltage of 10 mV in the frequency range 0.01 to 10⁶ Hz using a Solartron SI 1260 frequency response analyzer (Solartron, Hampshire, U.K.). Both real and imaginary components of the impedance were measured, and the real *z* axis intercept was closely approximated to provide an estimate of the membrane resistance, and hence, conductivity.

Theory

The proton conductivity in Nafion is strongly dependent upon its nanostructure and water content. At low water contents, not all acid sites are dissociated²⁵ and the interaction among water molecules via hydrogen bonding is low, resulting in a low dielectric constant and low rate of proton transfer, which is limited primarily to the surface region, providing very low conductivity. At high water contents, however, the properties of water in Nafion approach those of bulk water. Thus, two different water environments in Nafion have usually been distinguished.^{20,26,27} For instance, the water in the middle region of the pore is referred to as “bulk water,” through which the mobility of protons is fast. However, water near the pore surface along the array of SO_3^- groups is referred to as “surface water,” and the proton mobility through the surface is considerably smaller than that in the bulk, due to the strong electrostatic attraction of SO_3^- groups. Therefore, the measured proton conductivity of Nafion at given water content is the result of weighted average of the surface and bulk conductivities, depending upon the radial distribution of protons and water content in Nafion,²⁶ and can vary by two or more orders of magnitude as the RH is increased from dry conditions to saturations.

We assume that the transport of protons in Nafion is carried out via (i) a surface diffusion mechanism occurring close to the pore wall or under low water activity, *i.e.*, in a layer of around 1 nm from the pore wall,^{23,26} and (ii) a bulk diffusion mechanism prevailing in the central region of the pore or under high water activity con-

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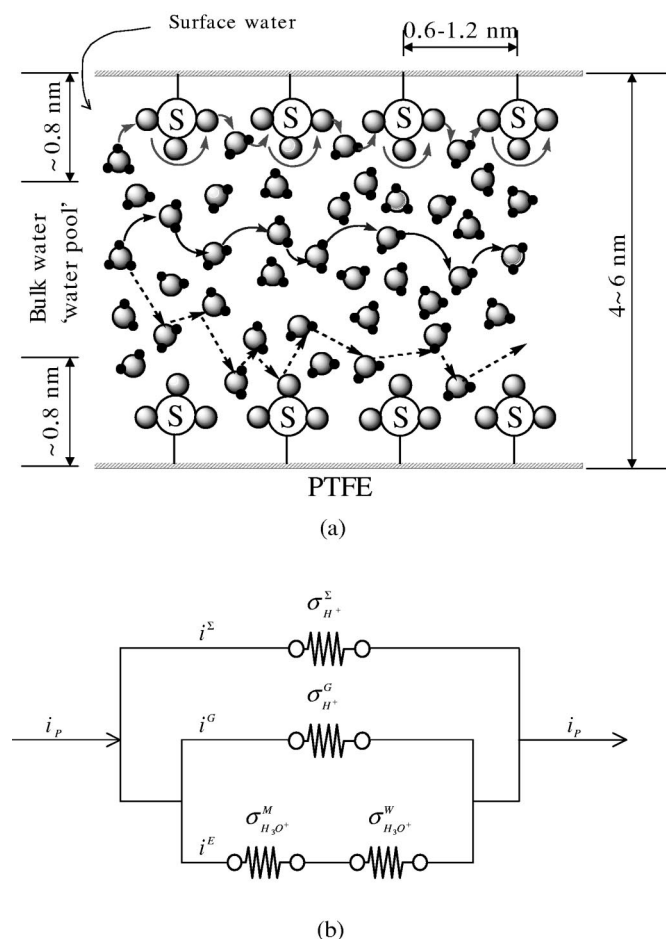


Figure 1. A simplified picture of structure and proton transfer in Nafion (a) in fully hydrated state and (b) electrical analog of the proton transport in Nafion.

dition.^{20,26-28} In the bulk, proton diffusion is predominantly via the Grotthuss mechanism, but the H_3O^+ ion also undergoes traditional mass diffusion,^{16,20,26-28} *i.e.*, the so-called *en masse* diffusion.

Figure 1 shows the various proton transport mechanisms along with an electrical analog. Thus, the proton conductivity in a pore σ_p can be written as

$$\sigma_p = \sigma_{\text{H}^+}^{\Sigma} + \sigma_{\text{H}^+}^{\text{G}} + \sigma_{\text{H}^+}^{\text{E}} \quad [1]$$

where $\sigma_{\text{H}^+}^{\Sigma}$, $\sigma_{\text{H}^+}^{\text{G}}$, and $\sigma_{\text{H}^+}^{\text{E}}$ represent the contributions of proton conductivity from the surface, Grotthuss, and *en masse* diffusion mechanisms, respectively.

The proton conductivity can be written in terms of diffusion coefficient using the Nernst-Einstein relation^{29,30}

$$\sigma_{\text{H}^+}^{\alpha} = \frac{F^2}{RT} D_{\text{H}^+}^{\alpha} C_{\text{H}^+}^{\alpha} \quad [2]$$

For *en masse* diffusion, the diffusion coefficient can be written as³¹

$$\frac{1}{D_{\text{H}^+}^{\text{E}}} = \frac{x_w}{D_{\text{H}^+}^{\text{W}}} \left(1 + \frac{1-x_w}{x_w} \frac{D_{\text{H}^+}^{\text{W}}}{D_{\text{H}^+}^{\text{M}}} \right) \quad [3]$$

where x_w is the mole fraction of water in the membrane phase, and $D_{\text{H}^+}^{\text{W}}$, and $D_{\text{H}^+}^{\text{M}}$ are the Stefan-Maxwell diffusion coefficient of hydronium ion and bulk water in the pore, and hydronium ion and

the polymer matrix M, respectively.³² Because the water mole fraction in PEMs is high even at low activity, *e.g.*, $x_w = 0.67$ at activity $a_i = 0.1$, and quickly approaches 1, Eq. 3 may be simplified to

$$\frac{1}{D_{\text{H}^+}^{\text{E}}} \approx \frac{1 + \delta_c}{D_{\text{H}^+}^{\text{W}}} \quad [4]$$

where $\delta_c \equiv (D_{\text{H}^+}^{\text{W}}/D_{\text{H}^+}^{\text{M}})[(1-x_w)/x_w]$. Thus, the total proton conductivity in a pore within Nafion can be written in terms of diffusion coefficients, concentrations, and the ratio δ_c

$$\sigma_p = \frac{F^2}{RT} \left(D_{\text{H}^+}^{\Sigma} C_{\text{H}^+}^{\Sigma} + D_{\text{H}^+}^{\text{G}} C_{\text{H}^+}^{\text{G}} + \frac{D_{\text{H}^+}^{\text{W}}}{1 + \delta_c} C_{\text{H}^+}^{\text{W}} \right) \quad [5]$$

Next, to account for the tortuous nature of the pores and the reduced cross-sectional area available for proton transport, the parallel pore model^{33,34} is utilized. The effective diffusion coefficient for the membrane is thus obtained by multiplying the diffusion coefficient for a single pore by ε_i/τ , where $\varepsilon_i = \lambda_i/(\lambda_i + r)$, λ_i is the moles of water sorbed per acid site, r is the ratio of partial molar volume of membrane to that of water,^{3,31} and τ is the tortuosity factor.³⁵ Then, the overall membrane conductivity σ_{H^+} is

$$\sigma_{\text{H}^+} = \frac{\varepsilon_i}{\tau} \left[\frac{F^2}{RT} \left(D_{\text{H}^+}^{\Sigma} C_{\text{H}^+}^{\Sigma} + D_{\text{H}^+}^{\text{G}} C_{\text{H}^+}^{\text{G}} + \frac{D_{\text{H}^+}^{\text{W}}}{1 + \delta_c} C_{\text{H}^+}^{\text{W}} \right) \right] \quad [6]$$

Therefore, the total conductivity depends upon the structural characteristics represented by δ_c and τ , as well as the distribution of proton concentration between the surface ($C_{\text{H}^+}^{\Sigma}$) and the bulk regions ($C_{\text{H}^+}^{\text{W}}$) within the membrane, which in turn are determined by the acid strength of the functional groups. All these parameters are affected by the amount of water in the membrane as discussed in the following. The details of water sorption in the membrane were treated in Part I.³

Proton Diffusion Coefficients

According to the random-walk view of diffusion, the diffusion coefficient of proton is given by the Einstein-Smoluchowski equation^{36,37}

$$D_{\text{H}^+} = \frac{l^2}{\kappa \tau_D} \quad [7]$$

where κ is a constant dependent upon the dimensionality of random-walk ($\kappa = 2, 4, \text{ or } 6$ for a one-, two-, or three-dimensional walk, respectively), l is the mean step distance, and τ_D is the mean time between successive steps. The use of Eq. 7 does not necessarily mean protons transfer via a "hopping" mechanism.³⁶ In fact, we use this viewpoint to obtain the diffusion coefficient for all three mechanisms of proton conduction in Nafion, namely, surface, Grotthuss, and *en masse* diffusions.

Surface diffusion coefficient.—Figure 2 shows a schematic representation of the "surface" hopping of a proton by means of a series of hops between adjacent sulfonic acid sites. Because the distance between the ionic groups is too large (0.6-1.2 nm) for a proton to step directly from one SO_3^- to the next, it must hop via intermediate water molecules,^{19,23} represented by the distance l_{Σ} . In order for this to occur, the proton should possess adequate energy to surmount the energy of activation resulting from the electrostatic attraction between the sulfonic ion SO_3^- and the hydronium ion H_3O^+ . It is assumed that this is the rate-determining step (rds) due to strong coulombic attraction of ionic groups.²⁷ Any subsequent hops to other water molecules before reaching the next sulfonic acid group are assumed to be rapid.

For the two-dimensional surface diffusion, $\kappa_{\Sigma} = 4$, and the τ_D^{Σ} may be written as

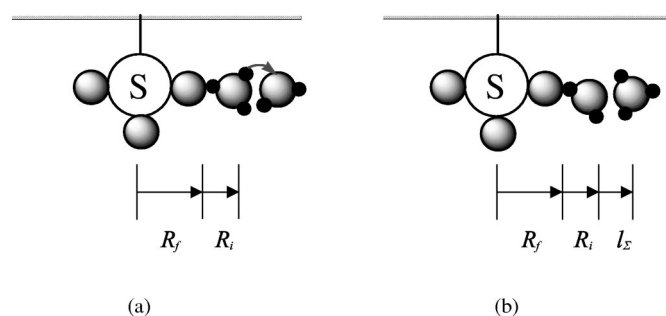


Figure 2. A schematic representation of the first proton hopping at the surface of Nafion (a) before and (b) after the first jump.

$$\tau_D^\Sigma = v_0^{-1} \exp\left(\frac{\Delta G_\Sigma^{e,0}}{k_B T}\right) \quad [8]$$

where the thermal frequency, $v_0 = k_B T/h$, and $\Delta G_\Sigma^{e,0}$ is the effective Gibbs free energy of activation for surface diffusion. The activation energy may include conformational fluctuation of potential barrier and the control of optimum conformation of the molecules participating in the proton transport near the surface of Nafion.² We assume here that the coulombic interaction energy between the negatively charged fixed sulfonic ion and the positively charged hydronium ion represents the main energy barrier. Then, the activation barrier for the first hop of a proton from a hydronium ion, closest to fixed sulfonic acid, to an adjacent water molecule is the coulombic energy between the fixed sulfonic ion and the positively charged hydronium ion minus the coulombic energy between the sulfonic ion and the new hydronium ion just formed after the first hop. Hence, the surface activation energy for the p th hop in a series of $p = 1, 2, 3, \dots, n$ proton steps starting from the hydronium ion adjacent to the fixed anion is²⁷

$$\Delta G_\Sigma^{e,0} = -\frac{(q_e^-)^2}{4\pi\epsilon_0\epsilon_r} \left[\frac{1}{R_f + R_i + p l_\Sigma} - \frac{1}{R_f + R_i + (p-1)l_\Sigma} \right] \quad [9]$$

where R_f is the effective radius of fixed anion groups, and R_i is the radius of the hydronium ion. Because the coulombic interaction energy decreases rapidly with the distance from the fixed anion site, and the dielectric constant of water is low in the surface layer, the first step is considered to be rate-determining for the overall surface proton hopping from one sulfonic acid site to the next. Substitution of $p = 1$ in Eq. 9 gives

$$\Delta G_\Sigma^{e,0} \approx \frac{(q_e^-)^2}{4\pi\epsilon_0\epsilon_r} \left[\frac{l_\Sigma}{(R_f + R_i + l_\Sigma)(R_f + R_i)} \right] \quad [10]$$

Clearly this analysis is simplified, because in reality, the coulombic interaction of adjacent sulfonic acid groups must also be taken into account. In fact, this results in a coulombic barrier that is sinusoidal.² Nonetheless, this does not invalidate the assumption that the first hop is the rds and successive hops between two neighboring sulfonic sites become easier. Combining Eq. 8 and 10 with Eq. 7 provides the surface diffusion coefficient for proton hopping in Nafion

$$D_{H^+}^\Sigma = \frac{k_B T}{h} \frac{l_\Sigma^2}{4} \exp\left[-\frac{(q_e^-)^2}{4\pi\epsilon_0\epsilon_r k_B T} \left\{ \frac{l_\Sigma}{(R_f + R_i + l_\Sigma)(R_f + R_i)} \right\} \right] \quad [11]$$

The radius of a hydronium ion R_i is taken as 0.143 nm based on the radius of water molecule $R_{H_2O} = 0.143-0.144$ nm,^{38,39} while the O-O distance between water molecules $d_{OO} = 0.275-0.294$ nm.⁴⁰⁻⁴² The radius of the fixed sulfonic acid R_f is 0.244-

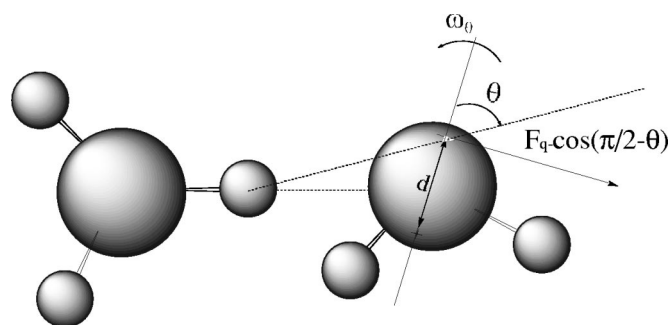


Figure 3. The hydrodynamic model of Grotthuss diffusion mechanism of protons in the pore bulk.

0.266 nm²⁴ accounting for the bond length of S-O in sulfonic acid $R_{SO} = 0.144-0.146$ nm,^{30,36,43} while the radius of negatively charged oxygen is about 0.10-0.12 nm.^{31,44,45} The distance between two oxygen atoms in both the Zundal ($H_5O_2^+$) and Eigen form ($H_9O_4^+$) is shorter, *i.e.*, 0.24-0.28 nm, than the O-O distance between water molecules as reported by molecular dynamic simulations.⁴⁶⁻⁵⁰ The hopping length l_Σ corresponds to the O-O distance in the proton hydrated forms and thus, l_Σ is taken as 0.255 nm. The dielectric constant of water in ionic solutions varies with the distance from the ions present in the solution.⁵¹⁻⁵⁴ Taking $R_f = 0.254$ nm, $R_i = 0.143$ nm, $\epsilon_r = 6$, and $l_\Sigma = 0.255$ nm gives the surface diffusion coefficient $D_{H^+}^\Sigma = 1.01 \times 10^{-7}$ cm²/s at room temperature. This is in good agreement with previous results.²⁰

Grotthuss diffusion coefficient.—In order to obtain the diffusion coefficient for the Grotthuss mechanism, it is assumed that the reorientation of the proton-accepting water molecule is the rds.⁹⁻¹³ This includes the 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 orientation. The proton transport itself following this rearrangement step is rapid. Agmon¹⁰ and recent MD simulations¹¹⁻¹³ support this step as the rds. The reorientation of the proton-receiving water molecule considered as a dipole is caused by the electrostatic field of the hydronium ion. Here, we present a solution for the Grotthuss diffusion coefficient based on classical treatment of water rotation and microhydrodynamics.

Figure 3 shows a schematic of the reorientation process due to the interaction between a charged ion (hydronium ion) and an adjacent water molecule considered as a dipole. Assuming that the excess charge is centered on the proton just prior to its transfer, the torque on the dipole at an orientation angle θ that tends to rotate the water molecule toward the hydronium ion is

$$T_\theta \approx -\frac{1}{4\pi\epsilon_r\epsilon_0} \frac{\mu_w(z_{H^+}q_e^-)}{\delta^2} \sin \theta \quad [12]$$

where μ_w is the dipole moment of water, and δ is the distance between the proton in hydronium ion and proton-accepting water molecule. Clearly, this represents a simplification of charge distribution on the hydronium ion as well as on the water molecule. A more sophisticated model might consider the water molecule as a quadrupole³⁰ and the hydronium ion with distributed excess charge on the three hydrogen atoms. The torque varies with θ , being the maximum at $\theta = \pi/2$

$$T_{\max} = \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{\mu_w(z_{H^+}q_e^-)}{\delta^2} \quad [13]$$

From hydrodynamics considerations, for a sphere of radius R_w rotating at an angular velocity ω_θ in a continuum fluid of viscosity η , the torque needed to maintain its rotation is given by Stokes equation^{35,55}

$$T_\theta = \zeta_{\text{rot}} \omega_\theta \quad [14]$$

where $\zeta_{\text{rot}} = 8\pi\eta R_w^3$ represents the rotational friction. The application of this to the rotation of a water molecule assumes that the viscosity of a fluid includes the effect of intermolecular forces such as hydrogen bond cleavage for the relative motion of fluid layers. Equating Eq. 12 with 14 and using Eq. 13 gives

$$\omega_\theta = -\frac{T_{\text{max}}}{\zeta_{\text{rot}}} \sin \theta \quad [15]$$

The angular velocity ω_θ is a function of the angle between the dipole moment vector and the ion. Assuming pseudosteady state, the time for the arrangement τ_D^G from an initial θ , θ_1 , to a final θ , θ_F , where proton transfer can occur, is

$$\tau_D^G = \int_{\theta_1}^{\theta_F} \frac{d\theta}{\omega_\theta} \quad [16]$$

Substituting Eq. 15 into 16 for ω_θ and integrating

$$\tau_D^G = \tau_C \ln \left[\frac{\tan(\theta_1/2)}{\tan(\theta_F/2)} \right] \quad [17]$$

where the characteristic time constant $\tau_C \equiv \zeta_{\text{rot}}/T_{\text{max}}$, *i.e.*

$$\tau_C = \frac{32\pi^2\eta\epsilon_0\epsilon_r R_w^3 \delta^2}{\mu_w(z_{\text{H}^+}q_{\text{e}^-})} \quad [18]$$

Thus, the proton hopping time for Grotthuss diffusion may be calculated *a priori* from Eq. 17 with parameters η , ϵ_r , R_w , δ , μ_w , θ_1 , and θ_F . The hydrodynamic radius of the water molecule is taken as $R_w = 0.141$ nm, and the distance of the proton of the hydronium ion and the water molecule is taken as $\delta = 0.143$ nm. The dipole moment of liquid water μ_w is typically⁵⁶⁻⁵⁸ 2.4-3.0 D (1 D = 3.336×10^{-30} C m) and is taken as $\mu_w = 2.95$ D based on recent calculations.^{59,60} According to the Conway, Bockris, and Linton (CBL) theory,^{9,61,62} the average angle of rotation required for the proton-accepting water molecule to rotate through for the favorable position is 105-111°. As shown in Fig. 3, the average initial angle of one of the sp^3 orbitals on oxygen is taken as 120°, or $\theta_1 = 2\pi/3$.⁹ Then, the final angle required for the proton transfer is $\theta_F = 9-15^\circ$, *i.e.*, $\theta_F = \pi/20-\pi/12$.⁹ Assuming this rearrangement of the proton-accepting water molecule as the rds, the mean time for arrangement τ_D^G corresponds to the mean hopping time for Grotthuss diffusion. This hopping time is not the same^{63,64} as the dielectric relaxation time, which is related to molecular rotation characteristic time.

Figure 4 shows the predicted Grotthuss hopping time τ_D^G for the variation of the angles suggested by Conway *et al.*^{9,61} The calculated hopping time τ_D^G at room temperature is in the range 1.40-1.68 ps, which agrees well with around 1.5 ps obtained from nuclear magnetic resonance (NMR) line narrowing measurement.^{65,66} The diffusion coefficient for Grotthuss mechanism $D_{\text{H}^+}^G$ can be calculated by taking $\kappa_G = 6$ in Eq. 7 and τ_D^G in Eq. 17 along with parameters described previously

$$D_{\text{H}^+}^G = \frac{l_G^2 \mu_w(z_{\text{H}^+}q_{\text{e}^-})}{192\pi^2\eta(\epsilon_r\epsilon_0)R^3\delta^2} \left/ \left[\ln \left[\frac{\tan(\theta_1/2)}{\tan(\theta_F/2)} \right] \right] \right. \quad [19]$$

The Grotthuss diffusion coefficient of $D_{\text{H}^+}^G \approx 7 \times 10^{-5}$ cm²/s is obtained for 107-108° rotation angle of the proton-accepting water molecule for $l_G = 0.255$ nm, which is the distance between O-O of proton hydrated molecule. Although this model is rather simple, it captures the essence of the phenomenon and provides insights into the Grotthuss diffusion mechanism, predicting a rea-

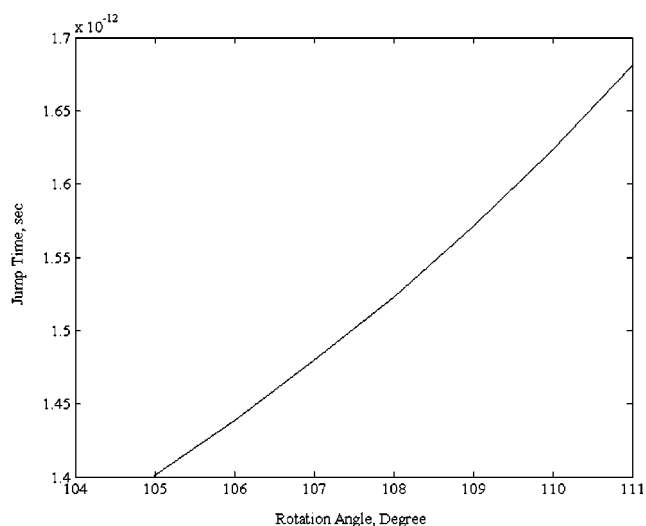


Figure 4. The Grotthuss hopping time for the variations of rotation angle of the proton-accepting water molecule.

sonable value for the Grotthuss diffusion coefficient of proton transport in the bulk water. Furthermore, it is consistent with Walden's rule, *i.e.*, $D\eta \equiv \text{constant}$. This theoretical framework may be further improved, for instance, by accounting for other interaction forces such as attractive and repulsive interaction by the Lennard-Jones model,^{31,36} electrostatic charge distributions among hydrogen atoms in the hydronium ion, and the quadrupole nature of water molecules.

En masse diffusion.—The *en masse* diffusion coefficient of hydronium ion may be calculated by the Stokes-Einstein equation, considering hydronium ion as a diffusing entity a continuum of water

$$D_{\text{H}^+}^W = \frac{k_B T}{6\pi\eta R_i} \quad [20]$$

where η is the viscosity of the medium and R_i is the radius of hydronium ion. In light of the Einstein-Smoluchowski equation,⁶⁷ the mean step time τ_D^E for three-dimensional *en masse* diffusion can be written as³⁸

$$\tau_D^E = \frac{\pi\eta R_i l_E^2}{k_B T} \quad [21]$$

where l_E is the mean step length for the *en masse* diffusion. Because the hydronium ion moves as a whole, the mean step length is taken as $l_E = 0.28$ nm, the O-O distance between two water molecules. The mean step time $\tau_D^E = 7.63$ ps is obtained for the *en masse* diffusion of hydronium ion from Eq. 21. Substitution of $\kappa_E = 6$, $\tau_D^E = 7.63$ ps, and $l_E = 0.28$ nm in Eq. 7 gives the diffusion coefficient for *en masse* diffusion $D_{\text{H}^+}^W = 1.71 \times 10^{-5}$ cm²/s. This is a reasonable value because the diffusion coefficient for *en masse* diffusion is frequently approximated by the self-diffusion coefficient of water, which has been reported as $2.26-2.3 \times 10^{-5}$ cm²/s in the literature.^{36,68}

Table I summarizes the mean step time and mean step distance for the surface, Grotthuss, and *en masse* diffusion mechanisms within the framework of the Einstein-Smoluchowski relation. The mean step time is smallest for the Grotthuss mechanism, indicating the Grotthuss diffusion is the fastest proton transport mechanism within Nafion. The mean step time for the surface diffusion is much

Table I. The mean step time and distance of the three diffusion mechanisms in the Einstein-Smoluchowski equation.

	Surface diffusion	Grotthuss diffusion	En masse diffusion
Step time, τ_D	1.61×10^{-9} s	1.5×10^{-12} s	5.78×10^{-12} s
Step distance, l	0.255 nm	0.255 nm	0.28 nm

higher than that of the other two mechanisms and thus, the surface diffusion does not contribute significantly to the overall conductivity of protons except at low water levels where it is the dominant mechanism. This also explains why the proton conductivity is low at low water content, because protons transfer mostly via the surface diffusion mechanism, which is slower by two orders of magnitudes.

The diffusion coefficient ratio, δ_c .—An alternative interpretation of the Einstein-Smoluchowski relation is to define l/τ_D as a mean velocity of hydronium ion between successive collisions. From Eq. 7

$$D_{H^+}^W = \frac{1}{\kappa} l_E \bar{v}_i \quad [22]$$

where \bar{v}_i is the mean speed of hydronium ions and l_E may be viewed as the mean-free path between successive collisions, in the spirit of the kinetic theory.^{36,69}

Based on the analogy, the parameter δ_c is estimated as follows. Using $x_w \approx \lambda_i/(\lambda_i + 1)$ in Eq. 4, δ_c may be rewritten as

$$\delta_c = \frac{1}{\lambda_i} \frac{D_{H^+}^W}{D_{H^+}^M} \quad [23]$$

The parameter δ_c can be interpreted as the ratio of Stefan-Maxwell diffusion coefficients, $D_{H^+}^W$ and $D_{H^+}^M$. Applying the expressions from elementary kinetic theory^{36,69} for the parameter l_E and \bar{v}_i to Eq. 22 and substituting the results into Eq. 23 provide

$$\delta_c = \frac{1}{\lambda_i} \left(\frac{d_{H^+M}}{d_{H^+W}} \right)^2 \left(\frac{m_{H^+M}^*}{m_{H^+W}^*} \right)^{1/2} \quad [24]$$

where d_{ij} is the distance between the centers of the spheres i and j when the collision occurs, and m_{ij}^* represents the reduced molecular mass of i and j , $1/m_{ij}^* = 1/m_i + 1/m_j$.^{36,69} Because $m_{H_3O^+} \approx m_W$ and $m_M \gg m_W$, the reduced molecular mass is $1/m_{H^+W}^* = 1/m_{H_3O^+} + 1/m_W \approx 2/m_W$ and $1/m_{H^+M}^* = 1/m_{H_3O^+} + 1/m_M \approx 1/m_W$. Substitution of this into Eq. 24 and use of $d_{H^+M}/d_{H^+W} \approx (\bar{V}_M/\bar{V}_{H_3O^+})^{1/3} \approx (\bar{V}_M/\bar{V}_{H_2O})^{1/3}$ gives

$$\delta_c = \frac{\sqrt{2}}{\lambda_i} (r)^{2/3} \quad [25]$$

where r is the ratio of partial molar volume of Nafion to that of water. Thus, the ratio δ_c depends upon the equivalent weight (EW) and water content in Nafion.

We now have predictive relations for all the parameters in Eq. 6, except for $C_{H^+}^{\Sigma}$ and C_{H^+} , which are discussed below.

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 comprising of Grotthuss and *en masse* mechanisms. The hydronium layer near the sulfonic ion SO_3^- is much like the inner Helmholtz layer, in which the water and hydro-

num ions are bound tightly to the fixed anion groups. The concentration of protons in this layer may be obtained by the electrical diffuse double-layer approach,⁷⁰ in which, for instance, the hydronium ions within 1 nm from the surface may be regarded as surface protons.

Here, we follow an alternative approach in which the dissociated acid sites with up to two water molecules are assumed to remain close to the surface and are designated as surface water, while those with more than two water molecules are assumed to move away from the surface into the pore bulk. This is based on the hypothesis that sulfonic acid groups are sufficiently strong acids so that ion pairs $SO_3^-H_3O^+$ or $SO_3^-H_5O_2^+$ are formed.² In reality, the nature of the backbone polymer affects this distribution of the water.

The balance of acid site gives³

$$\theta_0 + \theta_1 + \theta_2 + \theta_3 \dots = \theta_0 + \theta_1 + \theta_2 + \theta_{>2} = 1 \quad [26]$$

where θ_j denotes the fraction of acid sites with j bound water molecules. Using $\theta_j = K_j \theta_{j-1} a_i = \prod_{p=1}^j K_p \theta_0 a_i^j$ in Eq. 26 provides

$$\theta_0 = \frac{1}{1 + \sum_{j=1}^{\infty} (\prod_{p=1}^j K_p) (a_i)^j} \quad [27]$$

Because $K_1 > K_2$ and assuming $K_j = 1$ for $j > 2$, Eq. 27 reduces to

$$\theta_0 \approx \frac{1 - a_i}{(1 - a_i)(1 + K_1 a_i) + K_1 K_2 a_i^2 (1 - a_i^{v-1})} \quad [28]$$

Further with $\theta_1 = K_1 a_i \theta_0$, $\theta_2 = K_1 K_2 a_i^2 \theta_0$, $\theta_{>2} = 1 - \theta_0 - \theta_1 - \theta_2$, and $C_{H^+,0} = 1/(\lambda_i \bar{V}_i)$, the concentration of surface protons $C_{H^+}^{\Sigma} \approx C_{H^+,0}(\theta_1 + \theta_2)$ is thus

$$C_{H^+}^{\Sigma} = \frac{1}{\lambda_i \bar{V}_i} \frac{K_1 a_i (1 - a_i) (1 + K_2 a_i)}{(1 - a_i)(1 + K_1 a_i) + K_1 K_2 a_i^2 (1 - a_i^{v-1})} \quad [29]$$

while that of bulk protons $C_{H^+} \approx C_{H^+,0} \theta_{>2}$ is

$$C_{H^+} = \frac{1}{\lambda_i \bar{V}_i} \frac{K_1 K_2 a_i^3 (1 - a_i^{v-2})}{(1 - a_i)(1 + K_1 a_i) + K_1 K_2 a_i^2 (1 - a_i^{v-1})} \quad [30]$$

The equilibrium constants K_1 and K_2 are taken as 1000 and 200,³ respectively, based on the dissociation constant of sulfonic acid^{71,72} and the proton affinity data.⁷³ Thus, the surface proton concentration is high at low water content and then decreases as the water content increases for a given EW, while the bulk concentration increases monotonically with water content.

Tortuosity Factor

The tortuosity of a PEM depends upon the porosity ε_i or volume fraction of water. Several expressions for tortuosity have been proposed for porous media and membranes based on the statistical analysis of diffusion coefficients,⁷⁴ free volume theory,⁷⁵ and power series expansion,⁷⁶ etc. These models provide similar values of tortuosity factors for Nafion for the sorption range of interest. Here, we adopt Preger's model,⁷⁴ which has been previously used⁷⁶ for Nafion

$$\tau = \frac{2(1 - \varepsilon_i) + 2\varepsilon_i \ln \varepsilon_i - 0.5\varepsilon_i (\ln \varepsilon_i)^2}{\varepsilon_i (1 - \varepsilon_i) + \varepsilon_i^2 \ln \varepsilon_i} \quad [31]$$

The tortuosity τ depends on the water content ε_i , which in turn varies with water vapor activity (or RH) and EW.

Results and Discussion

Figure 5 shows the conductivity data^{77,78} of Nafion (EW 1100) at room temperature as a function of activity of water vapor along with

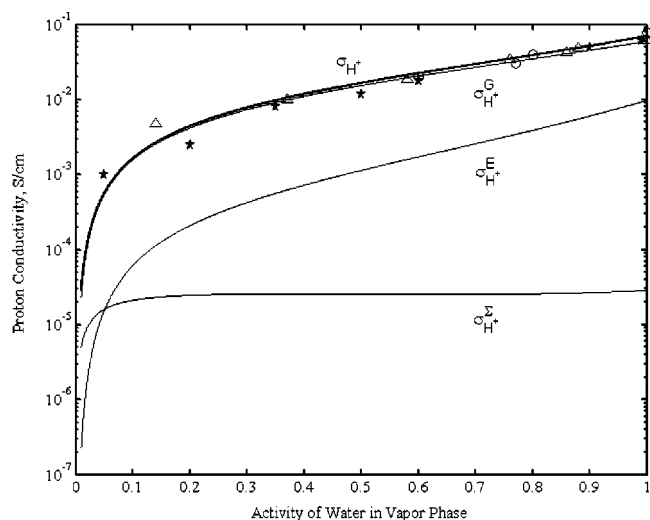


Figure 5. Proton conductivity of Nafion of EW 1100: (○) Ref. 79, (△) Ref. 80, (★) this work, and (—) model predictions.

the model predictions from Eq. 6 with Eq. 31 for τ , Eq. 11 for $D_{H^+}^{\Sigma}$, Eq. 19 for $D_{H^+}^G$, Eq. 20 for $D_{H^+}^W$, Eq. 25 for δ_c , Eq. 29 for $C_{H^+}^{\Sigma}$, and Eq. 30 for C_{H^+} . In addition, ε_i as a function of water activity is predicted as described in Part I.³ It is noteworthy that the predictions in Fig. 5 involve no fitted parameters. Thus, the total proton conductivity in Nafion is the result of three contributions: (i) $\sigma_{H^+}^G$, surface conductivity via proton hopping, (ii) $\sigma_{H^+}^E$, bulk conductivity via Grotthuss diffusion, and (iii) $\sigma_{H^+}^M$, bulk conductivity via *en masse* diffusion. Except for low activity of water vapor, the Grotthuss diffusion in the bulk is the dominant contributor to the total conductivity. At low activity the surface fraction of the water is dominant, e.g., more than 90% of water within Nafion is surface water at $a_1 = 0.1$ and thus, the total proton conductivity is quite low, but not zero as assumed in percolation models, due to the high activation barrier for hopping of surface protons.

Figure 6 compares the conductivity measurements of EW = 960 with the model. For EW = 960, the proton conductivity is higher compared to that for EW = 1100 at the same water vapor activity because volume fraction of water increases and the tortuosity de-

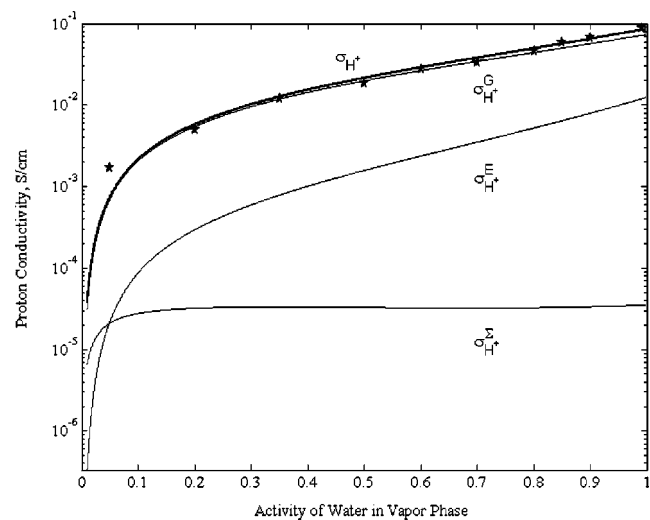


Figure 6. Comparison of proton conductivity data of Nafion of EW 960 with the model.

Table II. Comparison of the theoretical and experimental values of proton conductivity for various EWs of Nafion.

Equivalent weight (EW)	Conductivity (S/cm) Theory	Conductivity (S/cm) Experiment	Deviation from theory (S/cm)	Tortuosity Eq. 31
800	0.091	0.093	2.0×10^{-3}	1.30
900	0.115	0.116	1.0×10^{-3}	2.29
1000	0.100	0.114	1.4×10^{-2}	2.63
1100	0.086	0.090	4.0×10^{-3}	2.98
1200	0.068	0.065	3.0×10^{-3}	3.85

creases correspondingly, which facilitates the proton transfer through the pore. Similar to the case of EW = 1100, the Grotthuss diffusion controls the total conductivity of protons in the hydrated Nafion.

The effect of EW is examined by comparing the proton conductivity predicted by the model with experiments for Nafion of EW in the range of 800-1200 immersed in liquid water. Table II shows the proton conductivity of Nafion swollen in liquid water at room temperature predicted by the model along with the experimental results of Doyle *et al.*^{79,80} The model estimates the proton conductivity well over the range of EW. The maximum conductivity of Nafion predicted by the model is between EW of 900 and 1000, which is also obtained in experimental measurements. For EW less than 900, the proton conductivity decreases because the dilution effect of protons at low EW overwhelms the increase due to increase of water volume fraction and the corresponding decrease in tortuosity (Eq. 31).

In summary, the proton conductivity depends on the porosity ε_i , i.e., the volume fraction of sorbed water, tortuosity τ , proton concentrations in the surface region $C_{H^+}^{\Sigma}$ and in the bulk C_{H^+} , diffusion coefficients for the surface $D_{H^+}^{\Sigma}$, Grotthuss $D_{H^+}^G$, and the *en masse* mechanisms $D_{H^+}^W$, and the structural parameter δ_c . These also indicate the basic design variables that need to be optimized for developing alternative high-proton-conducting polymers for fuel cell applications. In general it is desirable to have PEMs that can sorb more water at a given water vapor activity, but only up to a certain point, when dilution effect on the proton concentration becomes significant. For a given PEM system, the membrane pores become larger and less tortuous when it sorbs large amounts of water, which in turn increases the conductivity of protons in the membranes. The factors that affect water sorption are discussed in Part I.³ The distribution of protons between the surface $C_{H^+}^{\Sigma}$ and the pore bulk C_{H^+} is also important and depends upon the acid strength of the functional groups as well as the nature of polymer backbone. Because the Grotthuss diffusion in the pore bulk is the major contributor to the total conductivity, the formation of a high fraction of bulk hydronium ions is required for the fast transfer of protons through the membrane. This may explain one of the reasons for the success of Nafion whose hydrophobic backbone facilitates the formation of bulk, rather than surface water. However, too high a water uptake in a PEM leads to a dilution of proton concentration and even membrane failure in an operating fuel cell. Especially for direct methanol fuel cell application, high water uptake and swelling may not be desirable due to the well-known methanol crossover problem.

Conclusions

A comprehensive proton transport modeling framework has been proposed here based on the understanding of various transport mechanisms in PEMs, such as surface hopping, Grotthuss diffusion, and *en masse* diffusion mechanisms, as well as the sorption characteristics of the membrane. The proton conductivity of PEMs depends on the water content and structural variables such as porosity, tortuosity, the ratio of diffusion coefficients δ_c , the distribution of protons, and the various diffusion coefficients for the proton conduction processes. The formation of high fraction of pore bulk water in PEMs is desirable for high conductivity because of the dominance

of Grotthuss diffusion mechanism in conductivity, which occurs in bulk water rather than at the surface. This may be a key reason for the success of Nafion, where surface hydrophobicity helps water cluster formation away from the surface. Most of the design variables of the proton conductivity model are related directly or indirectly to the amount of water in PEMs, which is the key variable in designing new PEMs. The transport model developed here provides a theoretical framework for understanding the proton transfer in PEMs and should also be helpful in systematically developing alternate high-proton-conducting PEMs for fuel cell applications as well as more fundamental, *e.g.*, *ab initio* or statistical mechanical prediction of diffusion coefficients.

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List of Symbols

a_i	activity of water vapor
C_{H^+}	concentration of protons in the pore bulk, mol/cm ³
$C_{H^+}^\alpha$	concentration of protons participating in the diffusion mechanism α , mol/cm ³
$C_{H^+}^\Sigma$	concentration of protons participating in surface diffusion, mol/cm ³
$C_{H^+}^E$	concentration of protons participating in <i>en masse</i> diffusion, mol/cm ³
d_{ij}	distance between the centers of the spheres i and j when collision occurs, nm
d_{H^+M}	distance between the centers of hydronium ion and matrix of membrane when collision occurs, nm
d_{H^+W}	distance between the centers of hydronium ion and water when the collision occurs, nm
$D_{H^+}^\alpha$	diffusion coefficient of protons for the diffusion mechanism α , cm ² /s
$D_{H^+}^E$	diffusion coefficient of protons for the <i>en masse</i> mechanism, cm ² /s
$D_{H^+}^G$	diffusion coefficient of protons for the Grotthuss diffusion mechanism, cm ² /s
$D_{H^+}^\Sigma$	diffusion coefficient of protons for the surface diffusion mechanism, cm ² /s
$D_{H^+}^M$	Stefan-Maxwell diffusion coefficient of protons and polymer matrix, cm ² /s
$D_{H^+}^W$	Stefan-Maxwell diffusion coefficient of protons and water, cm ² /s
$\Delta G_\Sigma^{e,0}$	effective Gibbs free energy of activation for surface diffusion, J/K
h	Planck constant, 6.626×10^{-34} J s
k_B	Boltzmann constant, 1.38×10^{-23} J/K
K_i	equilibrium constants for proton dissociation in membrane, dimensionless
l	mean step distance between steps, nm
l_Σ	mean step distance for surface diffusion, nm
l_G	mean step distance for Grotthuss diffusion, nm
l_E	mean step distance for <i>en masse</i> diffusion, nm
m_i	molecular mass of i , g
m_j	molecular mass of j , g
m_{ij}^*	reduced molecular mass of i and j , g
$m_{H^+M}^*$	reduced molar mass of hydronium ion and membrane, g
$m_{H^+W}^*$	reduced molar mass of water and membrane, g
p	jump steps starting from proton adjacent to the fixed anion, dimensionless
q_{e^-}	electrostatic electrons charge, 1.602×10^{-19} C
r	the ratio of partial molar volume of membrane to that of water, dimensionless
R	universal gas constant, 8.3144 J/(mol K)
R_f	effective radius of fixed anion groups, nm
R_i	radius of a component i (i = hydronium ion), nm
R_w	radius of a water molecule, nm
T	temperature, K
T_θ	torque on the dipole at an orientation angle θ , J
T_{max}	maximum torque, J
\bar{V}_M	molar volume of membrane, cm ³ /mol
\bar{V}_{H_2O}	molar volume of water, cm ³ /mol
$\bar{V}_{H_3O^+}$	molar volume of hydronium ion, cm ³ /mol
x_w	mole fraction of water in the membrane phase, dimensionless
z_{H^+}	charge number of ion, dimensionless
Greek	
δ	distance between the proton in hydronium ion and proton-accepting water molecule, nm
δ_c	concentration-dependent Stefan-Maxwell diffusion ratio, dimensionless
ε_i	porosity of the membrane, dimensionless
ε_0	permittivity of free space, 8.854×10^{-12} C ² /J/m
ε_r	relative permittivity of the medium, dimensionless
ζ_{rot}	rotational friction, J s
θ	orientation angle, dimensionless
θ_I	initial angle between diffusing proton and adjacent water molecule, dimensionless
θ_F	final angle diffusing proton and an adjacent water molecule, dimensionless
θ_j	fraction of acid sites with j bound water molecules, dimensionless
κ	dimensionality constant of random-walk, dimensionless

κ_E	dimensionality constant of <i>en masse</i> diffusion, dimensionless
κ_G	dimensionality constant of Grotthuss diffusion, dimensionless
κ_Σ	dimensionality constant of surface diffusion, dimensionless
λ_i	the moles of water sorbed per acid site, dimensionless
μ_w	dipole moment of liquid water, C m
ν_0	thermal frequency, 1/s
σ_p	proton conductivity in a pore of membrane, S/cm
$\sigma_{H^+}^\Sigma$	proton conductivity in the surface of membrane, S/cm
$\sigma_{H^+}^G$	proton conductivity by Grotthuss diffusion in the membrane, S/cm
$\sigma_{H^+}^E$	proton conductivity by <i>en masse</i> diffusion in the membrane, S/cm
τ	the tortuosity factor, dimensionless
τ_C	characteristic time constant, dimensionless
τ_D^E	mean time between successive jumps, ps
τ_D^G	mean time between successive jumps of <i>en masse</i> diffusion, ps
τ_D^E	mean time between successive jumps of Grotthuss diffusion, ps
τ_D^Σ	mean time between successive jumps of surface diffusion, ps
ω_θ	angular velocity, radian/s

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