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Surface proton hopping conduction mechanism dominant polymer electrolytes created by self-assembly of bicontinuous cubic liquid crystals†

Takahiro Ichikawa, *a Takeshi Yamada, *b Nanami Aoki,a Yuki Maehara,a Kaori Sudaa and Tsubasa Kobayashi *a

For the development of the next generation of fuel cells, it is essential to create an innovative design principle of polymer electrolytes that is beyond extension of the existing strategy. In the present study, we focused on the surface hopping proton conduction mechanism where an activation energy for proton conduction is greatly reduced by decreasing the distance between SO$_3^-$ groups. Our gyroid nanostructured polymer film (Film-G), with a hydrophilic surface where the SO$_3^-$ groups are aligned densely and precisely, shows high proton conductivity of the order of 10$^{-2}$ S cm$^{-1}$ when the water content is about 15 wt%. We reveal that the high proton conductivity of Film-G is attributed to the exhibition of an extremely-fast surface hopping conduction mechanism due to the reduced activation energy barrier along the gyroid minimal surface. This finding should introduce a game-changing novel opportunity in polymer electrolyte design.

Introduction

Nafion, which was developed in the late 1960s by DuPont, is surely the most successful polymer electrolyte because of its advanced proton conductivity and high mechanical stability.1–3 Significant efforts have been made for several decades to develop proton conductive polymer electrolytes beyond Nafion;4 however, Nafion still reigns as the most commonly used polymer electrolyte membrane for fuel cells and some other applications.5 Proton conduction in Nafion can be understood using a simple 2D nanochannel model composed of a water nanochannel sandwiched between hydrophobic walls (Fig. 1a).5,6 There are three proton conduction mechanisms in the nanochannel. One is the Grotthuss mechanism,7 which is a mechanism to transport protons via the formation/cleavage of hydrogen-bonding networks of water molecules in the bulk water region, namely a water pool, in the center of the nanochannel. The second is the en masse diffusion mechanism, which is the mechanism whereby hydrated oxonium ions migrate in the water pool. The third one is the surface proton hopping conduction (SPHC) mechanism where there are proton hops (PHs) from an SO$_3^-$ site on the surface of the hydrophobic wall to the neighboring SO$_3^-$ site via bridging water molecules between them. The proton conductivities in each mechanism are represented by $\sigma^G$, $\sigma^E$, and $\sigma^S$, respectively. The total proton conductivity of the polymer electrolyte membranes is $\sigma = \sigma^G + \sigma^E + \sigma^S$. Because of the significantly high proton conductivity in the Grotthuss mechanism, it has been common sense that the construction of macroscopically-continuous water pools, to

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Fig. 1  (a) Schematic representation of a proton conductive water nanochannel with a thickness of several nanometers. Grotthuss conduction ($\sigma^G$) is the dominant proton conduction mechanism. It is a useful model for conventional proton conductive polymer electrolytes, such as Nafion. (b) Schematic representation of a proton conductive water nanosheet with a thickness of <1 nm. Surface proton hopping conduction ($\sigma^S$) is the dominant conduction mechanism. Electrostatic potentials in the plane parallel to the hydrophobic wall surface are described.

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enhance the contribution of $\sigma^G$, is the most important design principle for creating advanced proton conductive polymer electrolytes.

Here, we propose a totally new design principle departing from the common sense idea for the creation of proton conductive polymer electrolytes showing high proton conductivity. We focused on the theoretical foresight on the SPHC mechanism. In 2001, Eikerling et al. revealed that distances between the neighboring $\text{SO}_3^-$ groups ($\delta\text{SO}_3^-\text{SO}_3^-$) on a hydrophobic wall surface strongly influence the electrostatic potential barrier in a direction parallel to the hydrophobic wall surface, $\psi$ (Fig. 1a). According to their estimates, when $\delta\text{SO}_3^-\text{SO}_3^-$ = 15 Å, $\psi$ is about 30 kJ mol$^{-1}$ while it reduces exponentially to 2–3 kJ mol$^{-1}$ as $\delta\text{SO}_3^-\text{SO}_3^-$ decreases to 5 Å. Since $\delta\text{SO}_3^-\text{SO}_3^-$ values in Nafion are relatively large at approximately 12 to 20 Å, the $\psi$ in Nafion is considered to be very large and consequently the $\sigma^G$ of Nafion appears as a very small value. These insights have led many researchers to consider the SPHC mechanism to be trivial; however, we envision that the dense and highly periodic alignment of $\text{SO}_3^-$ sites on a continuous surface should enable an ultrafast SPHC mechanism with an extremely small electrostatic potential barrier, resulting in the exhibition of a high proton conductivity on the order of $10^{-2}$ to $10^{-1}$ S cm$^{-1}$, that is, comparable to $\sigma^G$ in Nafion and/or bulk water (Fig. 1b).

Recently, the number of studies on the design of advanced proton conductive materials focusing on the alignment of the $\text{SO}_3^-$ groups has been increasing. Moreover, there are some studies that focus on the importance of the SPHC mechanism. There are also some studies that have employed the potential utility of zwitterions as ion conductive materials. Even bearing these previous studies in mind, the present work is the first study in which high proton conductivity is induced solely by the SPHC mechanism with an extremely-small activation energy.

**Results and discussion**

Aiming for the construction of polymer electrolytes with a dense and highly periodic alignment of $\text{SO}_3^-$ sites for the SPHC mechanism, we focused on our previously-designed liquid-crystalline (LC) amphiphile GZ (Fig. 2a). GZ has an ability to co-organize into bicontinuous cubic (Cubbi) phases with some acids, such as bis(trifluoromethane)sulfonimide (HTf$_2$N) (Fig. 2b) and a small amount of water. In the Cubbi phase, all of the $\text{SO}_3^-$ groups of GZ are aligned on a 3D gyroid minimal surface (G-surface) in a cubic cell with a lattice parameter ($L_{\text{Cubic}}$) of approximately 9–10 nm. A significant point is that it is possible to preserve its unique molecularly assembled nanostructure by in situ polymerization, which yields a self-standing polymer film, Film-G, with gyroid nanostructures (Fig. 2c). We roughly calculated $\delta\text{SO}_3^-\text{SO}_3^-$ in Film-G containing X wt% of water (Film-G(X)) based on structural analysis and its physicochemical properties (Fig. S2f). $\delta\text{SO}_3^-\text{SO}_3^-$ in Film-G(16.4) was estimated to be roughly 5.9 Å (Fig. 2d and S3f), which is predominantly shorter than that in Nafion. This is a value for which one can expect the exhibition of an ultrafast SPHC mechanism with a very small electrostatic potential barrier, $\psi$.

We expect that SPHC mechanisms in Film-G with $\delta\text{SO}_3^-\text{SO}_3^-$ = 5.9 Å can be roughly classified into four types depending on the degree of hydration of the $\text{SO}_3^-$ groups (Fig. 3a–d). In the driest state, SPHC is composed only of very slow PHs due to the strong

![Fig. 2](image-url) (a) Molecular structure of amphiphilic zwitterion monomer GZ. (b) Preparation scheme for a gyroid nanostructured polymer film (Film-G). (c) A photograph of Film-G and 3D image of the gyroid nanostructure in Film-G. (d) 3D image of a cubic cell in Film-G. A water nanosheet is constructed along a gyroid minimal surface (G-surface) shown in blue. The positions of the $\text{SO}_3^-$ groups of GZ are displayed as orange spheres.

![Fig. 3](image-url) Schematic illustration of the SPHC mechanism on the G-surface in Film-G with various water contents: (a) in the driest state; (b) in low water content; (c) in moderate water content; and (d) in high water content.
electrostatic interaction between the $\text{SO}_3^-$ anion and a proton (Fig. 3a). In the low-water-content state, these PHs are slightly accelerated due to the hydration of the $\text{SO}_3^-$ groups that largely weakens $\text{SO}_3^-$–proton interactions, while the PH speed is still slow because $r_{\text{SO}_3^-\text{-SO}_3^-} = 5.9 \, \text{Å}$ is a large value for a proton to hop directly (Fig. 3b). A further increase in water content leads to the situation where two hydrated $\text{SO}_3^-$ groups are connected via bound water molecules. PHs via these hydrated $\text{SO}_3^-$ groups are greatly accelerated, while PHs via those with fewer bound water molecules are still slow (Fig. 3c). When the water content reaches a situation where all the $\text{SO}_3^-$ groups are connected by bound water molecules (Fig. 3d), all PHs are highly activated and an effective SPHC mechanism is enabled at a macroscopic scale. This expectation is consistent with the dependence of proton conductivity ($\sigma_{\text{ht}}$) of Film-G on water content that was reported in our previous study.19

When the SPHC is dominant in proton conductivity, its $\sigma_{\text{ht}}$ can be described by

$$\sigma_{\text{ht}} = \frac{e_i}{\theta} \frac{F^2}{RT} \left( D_h^S C_h^S \right)$$

(1)

where $F$ is Faraday’s constant, $R$ is the universal gas constant, $D_h^S \left( \text{cm}^2 \text{s}^{-1} \right)$ and $C_h^S \left( \text{mol cm}^{-3} \right)$ are the diffusion coefficient and the concentration of $H^+$ on the surface, $T(K)$ is temperature, $e_i$ (dimensionless) is the volume fraction occupied by water, and $\theta$ (dimensionless) is a tortuosity factor. Detailed discussion about these parameters is provided in the ESL.† We will discuss below whether the high $\sigma_{\text{ht}}$ of Film-G can be explained solely by the SPHC mechanism.

According to the view of random walk diffusion, $D_h^S$ is given by the Einstein–Smoluchowski equation22,23

$$D_h^S = \frac{\ell_s}{\kappa_\text{D}^2}$$

(2)

where $\kappa$ is a constant value that depends on the dimensionality of random proton hops, $\ell_s$ is the hopping length, and $\kappa^D$ is the mean jump time for a PH. $\kappa^D$ can be expressed as

$$\kappa^D = \nu_0^{-1} \exp \left( \frac{\Delta G_{\text{hv}}^0}{k_b T} \right)$$

(3)

where $\nu_0$ is the thermal frequency, $k_b$ is the Boltzmann constant, and $\Delta G_{\text{hv}}^0$ is the effective Gibbs free energy of activation for surface hops. $\nu_0$ is expressed as $\frac{k_b T}{h}$, where $h$ is Planck’s constant. The main component of $\Delta G_{\text{hv}}^0$ is the potential barrier in the SPHC mechanism.24 Assuming that the proton conduction in Film-G(X) is solely based on the SPHC mechanism, $\Delta G_{\text{hv}}^0$ was estimated to be 13.3 kJ mol$^{-1}$ for Film-G(15.2) using the experimental value of $\sigma_{\text{ht}} = 8.5 \times 10^{-3} \, \text{S cm}^{-1}$ (Tables S4 and SS†). To confirm the validity of $\Delta G_{\text{hv}}^0 = 13.3 \, \text{kJ mol}^{-1}$, we examined the activation energy ($E_a$) of Film-G(X). The temperature dependences of $\sigma_{\text{ht}}$ of Film-G(15.2), Film-G(9.9), and Film-G(6.0) are shown in Fig. 4 using an Arrhenius plot. The measurements were performed in a narrow temperature range of 30 to 40 °C under a constant relative humidity of 90% with the aim of reducing the change in water content during the measurements. $E_a$ was found to be 17.2 kJ mol$^{-1}$ for Film-G(15.2), which was close enough to $\Delta G_{\text{hv}}^0 = 13.3 \, \text{kJ mol}^{-1}$. Since there is a small increase in the water content in Film-G(15.2) upon heating from 30 to 40 °C when the sample is kept under RH = 90% due to the increase in the absolute humidity, $E_a = 17.2 \, \text{kJ mol}^{-1}$ is expected to be an overestimate. The exact value of $E_a$ should be slightly smaller than 17.2 kJ mol$^{-1}$, meaning that our estimate of $\Delta G_{\text{hv}}^0 = 13.3 \, \text{kJ mol}^{-1}$ is very reasonable. These results strongly support the validity of our assumption that the SPHC mechanism is solely-dominant for the proton conduction mechanism in Film-G(15.2). Conversely, larger values of $E_a = 26.8$ and 35.3 kJ mol$^{-1}$ were found for Film-G(9.9) and Film-G(6.0), respectively, with lower water contents. This can be explained by the situation, where the $\text{SO}_3^-$ groups are partially bridged with bound water molecules, as shown in Fig. 3c, and some PHs with slower speed exist along the G-surface. This indicates that a suitable amount of water molecules is required to exclude slow PHs and yield only fast PHs, leading to the exhibition of high proton conductivity at a macroscopic scale.

Here, we compare the estimated physical property values of Film-G with those of Nafion. Using the value of $\Delta G_{\text{hv}}^0 = 13.3 \, \text{kJ mol}^{-1}$, the $D_h^S$ of Film-G(15.2) is calculated to be 6.99 $\times$ 10$^{-6}$ cm$^2$ s$^{-1}$, which is 70 times larger than that in Nafion.24 The ultrafast SPHC in Film-G(15.2) is ascribed to the formation of a considerably reduced electrostatic potential barrier on the G-surface by the correlated barrier hopping model24 that was realized for the first time by creating a unique situation, where the $\text{SO}_3^-$ groups are placed on a continuous surface in a dense and highly-periodic manner.

The experimental results on the water composition dependence of the $\sigma_{\text{ht}}$ of Film-G indicated that it is necessary to introduce a suitable amount of water molecules on the $\text{SO}_3^-$-aligned surface to enable the SPHC mechanism with a reduced $\psi$. We expected that the elucidation of the water state, dynamics and their composition dependence should be a significant way to understand the proton conduction mechanism in Film-G(X). The state of water in Film-G(X) was examined by DSC measurements (Fig. 5 and S11†). The DSC thermograms on cooling are shown in Fig. 5. There is no exothermic peak corresponding to the crystallization of water when the water content X is 17.3 wt% or less, while a small exothermic peak is
observed when \( X = 22.2 \) wt\%. These results clearly suggest that the water molecules in Film-G(X) exist as non-freezing bound water at least when \( X \approx 17.3 \), suggesting that the ultrafast SPHC mechanism in Film-G(15.2) is assisted only by non-freezing bound water.

With the aim of further investigating the dynamics of water in Film-G(X), we focused on quasi-elastic neutron scattering (QENS) measurements. QENS is a powerful technique for investigating the dynamics of water molecules in the picosecond to nanosecond timeframe and Ångstrom length-scale due to the large incoherent scattering cross-section of hydrogen. It has been employed for various materials including Nafion to reveal the dynamics of water molecules in it.\(^{25,26}\) Unlike Nafion that is mainly composed of C, O, S, and F elements, Film-G contains many hydrogen atoms. Thus, to obtain information on the dynamics of the water molecules in Film-G, we planned to examine the difference between the QENS spectra of Film-G containing normal water (H\(_2\)O) and those of Film-G containing heavy water (D\(_2\)O). Two types of Film-G samples with moderate water content (9.0 wt\% [Film-G(9.0)]) and high water content (16.4 wt\% [Film-G(16.4)]) were prepared by putting them under controlled relative humidity conditions. Resultant polymer films contain 3.0 and 6.0 water molecules per SO\(_3\)~ group, respectively. Below they are described as Film-G/mH\(_2\)O (\( m = 3 \) and 6). Using D\(_2\)O, Film-G/mD\(_2\)O (\( m = 3 \) and 6) were also prepared.

QENS experiments were carried out for these four samples at 300, 280, 260, and 240 K. The same experiment was performed at 10 K for resolution. Contour maps of QENS data of Film-G/3H\(_2\)O and Film-G/3D\(_2\)O at 300 K are shown in Fig. 6a and b. X- and Y-axes are momentum transfer \((Q)\) and energy transfer \((\Delta E)\), respectively. \( \Delta E \) reflects the quantity of energy exchange between an incident neutron and the sample. If a sample shows a relaxation phenomenon, a broad peak is observed as QENS around the elastic position \((\Delta E = 0)\). The width of the QENS broadening is inversely proportional to the relaxation time.\(^{37}\) There is a strong sharp scattering intensity at \( \Delta E = 0 \), and a moderate broad scattering intensity centered at \( \Delta E = 0 \), indicating that elastic and quasi-elastic components exist in the films. To extract the information on water molecules in Film-G, a differential contour map between the two was created using a scaling factor derived from the weight ratio of the two samples in the dry state (Fig. 6c). In the differential contour map, a significant difference is found mostly only in the \( \Delta E = 0 \) region, indicating that the dynamics of the water molecules in Film-G/3H\(_2\)O have almost stopped or are slower than the timescale represented by the instrumental energy resolution. Conversely, completely different results were obtained when \( m = 6 \). The contour maps of the QENS data of Film-G/6H\(_2\)O and Film-G/6D\(_2\)O and their differential data are shown in Fig. 6d-f. It is noteworthy that a broad scattering intensity was found in Fig. 6f, indicating that there is a certain amount of mobile water molecules in Film-G/6H\(_2\)O.

To evaluate the dynamics of the water molecules in Film-G more quantitatively, we analyzed the QENS profiles of Film-G/mD\(_2\)O and Film-G/mH\(_2\)O (\( m = 3 \) and 6). The QENS profiles of \( m = 3 \) were integrated in the \( Q \) direction due to the small contribution from hydrated water. The obtained results were fitted by the following phenomenological equation

\[
S(Q, E) = \left\{ A_0 \delta(E) + \sum_{i=1}^{n} A_i L_i(G_i, E) \right\} \otimes R(Q, E)
\]  

where \( A_0 \delta(E) \) denotes the elastic component with coefficient \( A_0 \) and delta-function \( \delta(E) \), \( A_i \) is the coefficient of the \( i \)-th Lorentzian-function, \( L_i(G_i, E) \), where \( G_i \) is the half width at half maximum (HWHM) of the Lorentzian-function, and \( R(Q, E) \) refers to the instrumental resolution function, which was obtained at 10 K. Fig. 7a and b show fitting results for the QENS profile of Film-G/3D\(_2\)O and Film-G/6D\(_2\)O at \( T = 300 \) K. It is successfully fitted with the sum of a delta-function and two Lorentzian-functions (\( n = 2 \) in eqn (4)), which are drawn with lines in red, green, and blue, respectively. Since D\(_2\)O hardly contributes to the QENS profile, the observed QENS broadening reflects the dynamics of Film-G, namely the alkyl chain motion of GZ (Fig. S16–S18†). In contrast, the QENS profile of Film-G/mH\(_2\)O (\( m = 3 \) and 6) includes dynamics of not only Film-G but also mH\(_2\)O. This difference between Film-G/mH\(_2\)O and Film-G/mD\(_2\)O (Fig. 6c and f) leads us to consider that an additional Lorentzian-function, representing the mobile water molecules, is required for fitting of the QENS profile of Film-G/mH\(_2\)O.
Therefore, it was fitted by eqn (4) with three Lorentzian-functions \((n = 3)\), where parameters \(L_3\) and \(L_2\) corresponding to Film-G were fixed using the results of Film-G/6D2O, and the three parameters \(A_0\), \(A_3\), and \(L_3\) were adjusted. This approach substantially reproduced observed data (Fig. 7c and d).

In the case of \(m = 3\), the number of immobile and mobile hydrogen atoms \((N_{H(immob)}\) and \(N_{H(mob)}\)) in Film-G/3H2O was estimated as follows,

\[
N_{H(immob)} = \frac{A_0(\text{Film-G}/3H_2O) - A_0(\text{Film-G}/3D_2O)}{(A_0(\text{Film-G}/3H_2O) - A_0(\text{Film-G}/3D_2O) + A_3)} \times 12
\]

\[
N_{H(mob)} = \frac{A_3}{(A_0(\text{Film-G}/3H_2O) - A_0(\text{Film-G}/3D_2O) + A_3)} \times 12
\]

where 12 indicates the number of hydrogen atoms in the water molecules per GZ molecule. The obtained \(N_{H(immob)}\) and \(N_{H(mob)}\) are plotted in Fig. 8a. It is notable that immobile water predominates in Film-G/3H2O. In the case of \(m = 3\), the hydration degree on the G-surface is expected to be the situation shown in Fig. 3b or c. Therefore, many of the water molecules are fixed on the SO3 groups, while some of them near H+ are fluctuating.

In contrast, in the case of \(m = 6\), since it was revealed that a certain amount of the water molecules are in the mobile state, the Q dependence of the parameter \(L_3\) was examined to extract spatial information about the observed dynamics. The Q dependence of \(L_3\) at 300 K did not approach zero at \(Q = 0\) Å\(^{-1}\) (Fig. S20†). Although obtained data was scattered, \(L_3\) was found to be almost constant with respect to \(Q\). These results suggest that the observed dynamics corresponding to \(L_3\) is a local mode, such as rotation and/or local jumps of the water molecules. A similar trend was also observed at other temperatures. This means the scale of the localized mode is within a scale of several Ångstroms. For further consideration, the Q dependence of the elastic incoherent scattering factor (EISF) was calculated as follows,

\[
\text{EISF}(Q) = \frac{A_0(\text{Film-G}/6H_2O) - A_0(\text{Film-G}/6D_2O)}{(A_0(\text{Film-G}/6H_2O) - A_0(\text{Film-G}/6D_2O) + A_3)}
\]

The Q dependence of EISF, as plotted in Fig. 8b, was well reproduced by a diffusion model in the confined sphere, as follows,

\[
\text{EISF}(Q) = (1 - f_{mob}) + f_{mob} \left( \frac{3j_1(Qr)}{Qr} \right)^2
\]

where \(f_{mob}\) and \(r\) and \(j_1\) are the mobile fraction of hydrogen corresponding to water, the radius of the confined sphere, and a first-order spherical Bessel function, respectively. The value of \(r\) was 4.2 Å at 300 K (Fig. 8c), which covers enough neighboring sites of SO3 (\(j_{SO3,SO_3}\)). The space decreased with decreasing temperature. \(N_{H(immob)}\) and \(N_{H(mob)}\) were estimated from 24 × \((1 - f_{mob})\) and 24 × \(f_{mob}\), respectively (Fig. 8d). In contrast to Film-G/3H2O, the mobile water predominates in Film-G/6H2O. In the case of \(m = 6\), the degree of hydration reaches the
situation shown in Fig. 3d, where the presence of H+ causes not only the near water molecules to wobble but also distant ones connected through hydrogen-bonding networks, which consequently puts a large part of the water molecules in a mobile state.

The relaxation time of these mobile water molecules ($\tau_{\text{QENS}}$) was evaluated using the following formula,

$$\tau_{\text{QENS}} = \hbar \frac{1}{T_\gamma}$$  \hspace{1cm} (9)

where $\hbar$ is h/2$\pi$. The value $\tau_{\text{QENS}}$ was estimated to be 37 ± 4 ps at 300 K, which is of the same order as $\tau_\gamma$ calculated when assuming $\Delta G^{\text{OH}}_\text{H}_2 = 13.3$ kJ mol$^{-1}$ (Table S5†). Consistency of theoretical $\tau_\gamma$ and experimental $\tau_{\text{QENS}}$ is also found for results at other temperatures (Fig. 9). These results suggest that the dynamics of the mobile water molecules are deeply involved in the SPHC mechanism.

Conclusions

We have succeeded in demonstrating the potential utility of the surface proton hopping conduction (SPHC) mechanism for the development of advanced proton conductive polymer electrolytes. These findings will contribute to the development of advanced fuel cells, such as anhydrous-drive-type and/or low-temperature-drive-type ones. From a comprehensive viewpoint, present findings suggest that control over self-organization should be a key strategy for creating new functional materials that support next-generation technologies.

Data availability

The datasets supporting this article have been uploaded as part of the ESL.†

Author contributions

T. I. supervised this project. T. I. and T. K. designed materials. T. I., N. A., Y. M., K. S., T. K., and T. Y. performed the experiments and analyzed the data. T. I. and T. Y. wrote the manuscript. All authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references