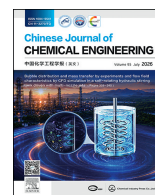




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Full Length Article

Molecular dynamics study on proton transport in Nafion, sulfonated polyethylene, and sulfonated poly(ether ether ketone) membranes

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ABSTRACT

Understanding the proton transport mechanisms in polymer electrolyte membranes (PEMs) is crucial for optimizing proton exchange membrane fuel cells. In this study, classical molecular dynamics simulations are employed to systematically investigate the proton transport behavior in three representative membranes: Nafion, sulfonated polyethylene (P21SA), and sulfonated poly(ether ether ketone) (SPEEK). The results reveal that proton transport in Nafion is dominated by the classical hopping mechanism (CHM), facilitated by the extensive free volume, well-connected water channels, and highly dynamic hydrogen-bond network. In contrast, SPEEK exhibits limited free volume and narrow-twisted water channels, which can suppress hydrogen-bond network reorganization. The proton transport in SPEEK is primarily governed by the vehicle mechanism. P21SA shows intermediate features between Nafion and SPEEK, displaying a hybrid transport mechanism. This study establishes direct correlations between nanoscale morphology, hydrogen-bond network dynamics, and proton transport behavior, providing molecular-level insights for the rational design of PEM materials.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) transform chemical energy into electric energy by electrochemical reactions [1,2]. The key components in PEMFCs include the electrodes, polymer electrolyte membrane (PEM), catalyst, and gas diffusion layers [3,4]. During the electrochemical reactions, the protons formed at the anode permeate through the PEM to the cathode side, while the electrons travel along an external load circuit, thus creating the current output for the fuel cell [5,6]. The proton transport mechanism in PEM directly determines the fuel cell's performance, efficiency, and lifespan [7]. Owing to the limitation of experimental techniques [8–12], it is difficult to fully elucidate

the specific proton transport mechanisms [13,14], microscopic states of protons [15], and transport channels [16] in the PEMs. The understanding of the proton transport mechanism remains mainly at the qualitative level [17].

Nafion, sulfonated poly(ether ether ketone) (SPEEK), and sulfonated polyethylene (P21SA) are the three widely used membranes in PEMFCs [18]. Nafion is a brand name of perfluorinated copolymer with containing hydrophilic ionic groups (sulfonic acid groups), which can attract water molecules [19,20]. The ionic groups are solvated, and the protons are dissociated from the sulfonate groups. The protons diffuse from one acid site to another along the chain backbone and hydrogen bonding network [20–22]. SPEEK and P21SA were developed to overcome the high cost and environmental unfriendliness of perfluorinated sulfonate PEMs [23]. They are the most promising alternatives to Nafion [24,25]. The sulfonated groups can also improve the membrane properties in terms of wettability, water flux, antifouling capacity, perm-selectivity and solubility in solvents [26]. The proton transport mechanism in these three membrane, particularly in P21SA and SPEEK, remains to be explored and clarified [27]. It is

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important to study the mechanism, which provides useful insights into the rational design. Recent experimental studies have demonstrated that tailoring hydrophilic functional groups can effectively construct continuous water networks, thereby significantly enhancing the proton conductivity. For example, proton transport can be significantly improved by the carboxyl-dominant water networks formed on two-dimensional metal-organic frameworks [28].

Proton transport mechanisms include the vehicle [29] and the Grotthuss mechanism [30]. In the vehicle mechanism, proton transport through the self-diffusion of proton carriers such as H_3O^+ and NH_4^+ , which moves along with the vehicles like H_2O and NH_3 [31]. In the Grotthuss mechanism, hydronium ions can form hydrogen bonds with surrounding water molecules, enabling the continuous hopping movement of protons through the formation/breakage of OH covalent bonds [32,33]. The proton transport in many cases [34–37] is more complex because of the influences of membrane microstructure, hydrogen bond networks (HBNs), and interactions between proton-carrier and membrane. For example, the proton conductivity can be significantly enhanced under the formation of smoothly-connected proton transport channels [38]. Meanwhile, the proton hopping rate is mainly determined by the rate of HBN reorganization, where high reorganization rate enhances the formation of proton transport channels [39]. For example, proton conduction is enhanced in covalent organic framework membranes, because of the proton transport channels determined by the high water-retentive capability [40]. When the HBNs are formed by multiple interaction sites, the proton conductivity and membrane stability can also be enhanced [41].

Available studies on the proton transport exhibited two main limitations [42,43]. Firstly, the full evolution dynamics of proton transportation in complex PEMs are not fully studied. Secondly,

there is a lack of quantitative description for the proton transportation in terms of the microstructure and the HBN dynamics. It remains a challenge to establish a precise relation between HBN characteristics and proton conductivity, which underscore the scientific urgency of further investigations. Molecular dynamics (MD) simulation is an important tool for investigating proton transport mechanisms in PEMs at the molecular level. The approach employed in this study utilizes classical MD and force fields. These force fields cannot capture the forming/breaking of covalent bonds in Grotthuss mechanism [14]. However, classical MD simulations have been extensively applied to elucidate the proton transport mechanisms in terms of hydronium ion diffusion and hydrogen-bond network dynamics [44–47]. It is noted that the hopping mechanism observed in classical MD simulations is resulted from the formation/breakage of hydrogen bonds in the network, which is distinct from the Grotthuss mechanism. To clarify this point, the hopping mechanism in classical MD simulations is named as classical hopping mechanism (CHM) in this work. In Grotthuss mechanism, protons diffuse in the hydrogen bond network through the formation/breakage of covalent bonds involving neighboring molecules, which is an interconversion between OH covalent bonds and hydrogen bonds. In CHM, protons hop because of the formation/breakage of hydrogen bonds in terms of hydronium ion diffusion, which is a completely physical diffusion process. In general, protons in the Grotthuss mechanism moves much faster than that in CHM.

In this work, we employed MD simulation to investigate the proton transport mechanisms in Nafion, SPEEK, and P21SA membranes. The relation between microstructure and proton transport properties is explored. The diffusion coefficients, membrane pore size, and free volume data are calculated to reveal both the static and dynamic properties of proton transport.

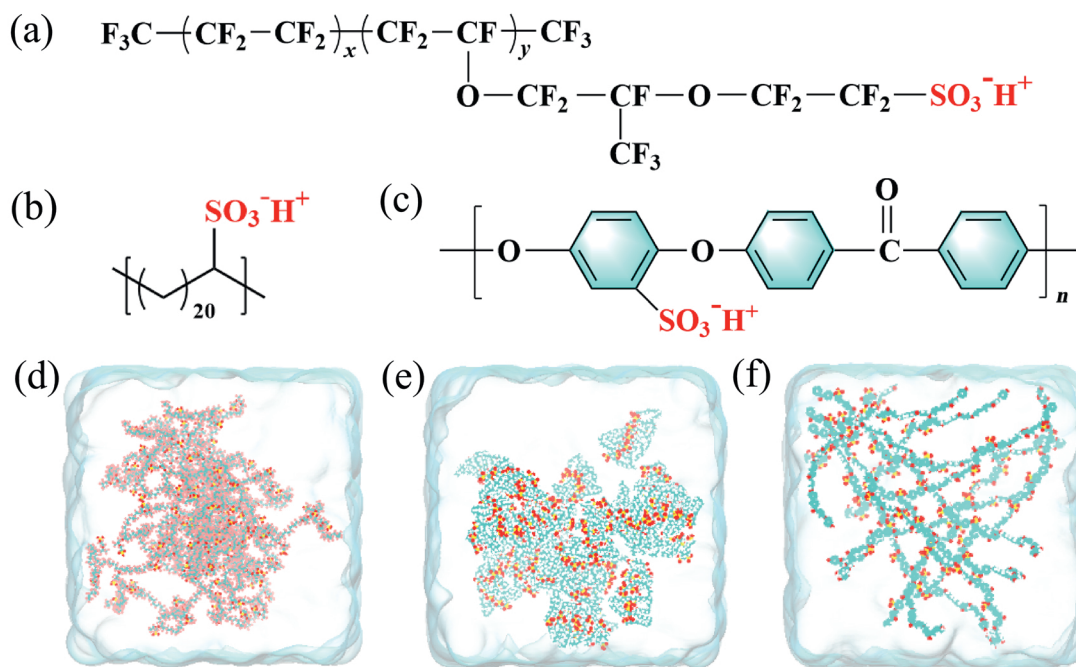


Fig. 1. The chemical structures of (a) Nafion, (b) P21SA, (c) SPEEK. (d)–(f) The snapshots for Nafion, P21SA and SPEEK membranes. The water molecules and hydronium ions are labeled by light blue color (background color). The carbon backbone and sulfonic acid groups are labeled by dark blue color and red color, respectively.

2. Simulation Methods

Simulation models for Nafion, P21SA, and SPEEK membranes are constructed using a single polymer chain composed of 10 repeated monomers ($n = 10$), as illustrated in Fig. 1(a)–(c). For the Nafion, each repeat unit comprises 10 difluoromethylene (CF_2) groups arranged in a configuration with $x = 7$ and $y = 1$ (Fig. 1(a)). Using Packmol software [48], the simulation mixtures are generated by randomly distributing 21 chains in a cubic simulation box of size $22 \text{ nm} \times 22 \text{ nm} \times 22 \text{ nm}$ (Fig. 1(d)–(f)). The hydration number (λ) for water molecules is set at 20 for most of the cases. When $\lambda > 20$, protons exist in a completely dissociated form and can be solvated as hydronium ions (H_3O^+) [49]. When λ is around 20, a continuous hydrogen-bond network can be formed within the membrane, which enables both the classical hopping and vehicle mechanism to operate effectively. Therefore, it is possible to explore how the membrane's microstructure favors one mechanism over the others.

Non-bonded interactions are described the Lennard-Jones and Coulombic potential. The total interaction energy is [50,51].

$$U = \sum_{ij} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where ϵ_{ij} and σ_{ij} represent the interaction energy and effective diameter, respectively. q_i is the partial charge of bead i . ϵ_0 is the vacuum permittivity. The summation is calculated over all beads in the system. The Coulombic interactions are calculated using the particle mesh Ewald (PME) method [52], while Lennard-Jones interactions are calculated with a cutoff distance of 1.5 nm with no shift.

Finally, some hydronium ions are introduced to neutralize the system, with the sulfonation level of SPEEK maintained at 70%. The polymer chains are modeled by the GAFF force field [53,54], while the water molecules are described by the TIP3P model [55]. The hydronium ions are described by the Kusaka model [56]. More details are listed in Table S3 in Supplementary Material. The applicability of the force field is verified by comparing the density with experimental and simulation data (see Table S1). To further validate the force field for dynamic properties, the diffusion coefficients of water and hydronium ions are also compared with other simulation data (Fig. 2(c and d)). Results show that the force field reasonably reproduces the data.

The all-atom MD simulations were performed using the GRO-MACS V5.0.6 package [57,58]. Initially, energy minimization was performed, followed by a multi-step annealing procedure [47]. First, the systems were equilibrated under NPT conditions at 300 K and 100 bar to gradually compress them to the experimental

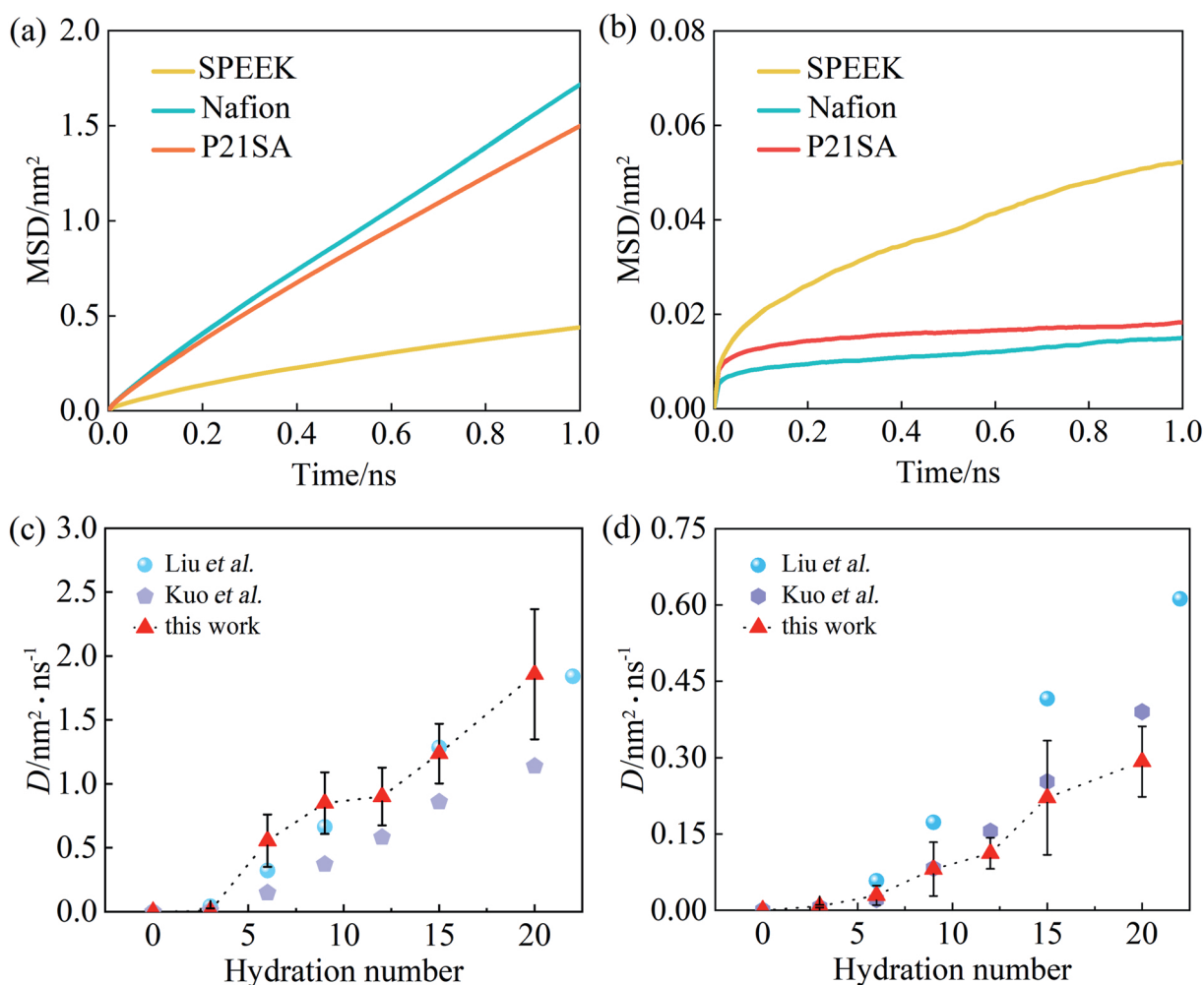


Fig. 2. (a) MSD of hydronium ion. (b) MSD of sulfonate groups in the polymer chain. (c) Diffusion coefficient of water molecules in Nafion. (d) Diffusion coefficient of hydronium ions in Nafion. The reference data are adopted from Refs. [64,65].

density, after which the conditions were reset to 300 K and 0.1 MPa for an additional NPT simulation. Subsequently, a constant-volume simulation of 5 ns was conducted, during which the temperature was increased in 500 ps intervals up to 800 K and then decreased to 300 K using the same time intervals. Then, the system was immediately conducted another 5 ns NPT simulation at 300 K and 0.1 MPa. This cyclic annealing process was repeated four times to ensure that the system density reached a stable value. An NPT simulation was conducted at 300 K and 0.1 MPa for 100 ns to equilibrate the chain conformations (see Fig. S1). All the diffusion data are calculated in NVT ensemble with simulations of 25 ns. Temperature and pressure were maintained using the Nosé-Hoover thermostat [59] and an isotropic Parrinello-Rahman barostat [60,61], respectively. A time step of 1 fs was used for all simulations. All of the data presented in this work are the ensemble average over three independent trajectories.

3. Results and Discussion

3.1. Diffusion properties

To gain insights into the proton transport mechanism at the molecular level, it is critical to analyze the mobility of the key species involved. In this work, the dynamic behavior of hydronium ions and sulfonate groups is examined as a function of time. To elucidate the molecular dynamics of hydronium ions and sulfonate groups within the membranes, the mean square displacement (MSD) of these species is calculated for the three membranes. The MSD provides a quantitative measure of molecular mobility by evaluating the average displacement of one molecule in the simulation. Fig. 2 presents the MSD data for hydronium ions and sulfonate groups in the three membranes.

In the SPEEK system, sulfonate groups exhibit high mobility. Concurrently, the relatively low proton mobility indicates that proton migration is largely dependent on the vehicles, proceeding through the cooperative diffusion of the sulfonate groups and hydronium ions [29]. This interpretation is consistent with studies by classical MD [21], which found that the hydronium diffusivity in SPEEK is lower than in Nafion with one order of magnitude, due to the more pronounced electrostatic attraction.

Protons primarily diffuse along the carriers of sulfonate groups or water molecules. Consequently, the high mobility of sulfonate groups directly facilitates proton transportation. In contrast, the sulfonate groups in Nafion exhibit low mobility, while the protons have the highest diffusion coefficient [21,62,63]; see Table 1 and Fig. 2(a)–(b). While our simulations capture the vehicle transport, the high overall conductivity can be attributed to the dominance of the CHM. This indicates that proton transport relies more on the rearrangement of hydrogen-bond networks than on the movement of sulfonate groups. The mobility of sulfonate groups and protons in P21SA lies between that of Nafion and SPEEK. The microstructure contains both continuous water channel regions related to rapid proton hopping and isolated water cluster regions related to the vehicle mechanism. To ensure the simulation reliability, the diffusion coefficients of protons and water molecules at different λ are also calculated and compared with the simulation data in literature [64,65]; cf. Fig. 2(c)–(d). In addition, the system

density and the position of the first peak in radial distribution function (RDF) are compared with the experimental/simulation data in literature [54,64,66,67]; see Tables S1 and S2. All of the results show good agreement.

3.2. Radial distribution function

Building on the previous analyses, the next step is to probe the microscopic interactions that facilitate proton transport by examining the RDF of critical species. Specifically, the RDFs for sulfonate-hydronium ($\text{SO}_3\text{-H}_3\text{O}^+$) and water-water ($\text{H}_2\text{O-H}_2\text{O}$) pairs are calculated in the Nafion, P21SA, and SPEEK membranes.

The hydrogen bond network structure is pivotal in influencing the transport mechanism. As shown in Fig. 3(b), the RDF of $\text{H}_2\text{O-H}_2\text{O}$ in Nafion has the highest value with a coordination number more than 4.5 (cf. Table S4). It indicates the formation of the most extensive and continuous hydrogen bond network within Nafion. This result is also consistent with previous experimental study. The highly-connected hydrated nanochannel structure in Nafion is critical for achieving high proton conductivity [68]. The strong $\text{H}_2\text{O-H}_2\text{O}$ interaction energy (Fig. 3(d)) further corroborates this conclusion. This highly connected HBN may provide an ideal pathway for rapid proton migration along HBNs by CHM. In contrast, SPEEK has a low coordination number (about 3.6) for water-water interactions (see Table S4), as well as a weak interaction energy (Fig. 3(d)). It means that water molecules probably exist as isolated water clusters, forming poor-connected HBNs, so that suppresses the proton hopping. Consequently, protons primarily transport by the vehicle mechanism.

The corresponding value for P21SA lies between the two, suggesting the water network structure exhibits transitional features. Fig. 3(a) shows the RDF for the $\text{SO}_3\text{-H}_3\text{O}^+$ pairs, revealing a sharp peak at approximately 0.31 nm. The values of these peaks are significantly higher than those observed for the $\text{H}_2\text{O-H}_2\text{O}$ pairs in Fig. 3(b). This pronounced difference is attributed to the strong electrostatic non-bonded interactions between the hydronium ions and the negatively charged sulfonate groups [69]. Furthermore, the gradual decrease in the sharpness of these peaks indicates a reduction in the number of sulfonate groups surrounded by hydronium ions. A quantitative analysis on the local proton coordination further reveals that approximately 57% of protons are associated with sulfonate groups, while 43% reside in aqueous environments. This data also provides direct support for the hybrid transport mechanism.

SPEEK exhibits a higher coordination number for $\text{H}_3\text{O}^+ - \text{SO}_3^-$ than Nafion, while P21SA has the highest value. This reveals a more concentrated distribution of sulfonate groups in SPEEK and P21SA, forming a high concentration of protons. However, within the SPEEK, despite the abundance of local proton carriers, narrow water channels impede proton hopping. Consequently, proton transport primarily relies on the overall diffusion of these carriers within the confined spaces. In contrast, Nafion possesses slightly less proton carriers bonded to individual sulfonate groups. The water network enables efficient hopping through HBNs once protons are dissociated. The high coordination number of $\text{H}_3\text{O}^+ - \text{SO}_3^-$ and well-connected HBNs in P21SA are the evidence for the hybrid mechanism in proton transport. Some protons can hop within the network, while other ones diffuse along the hydronium ions.

3.3. Membrane internal structure

To further quantify the structural influences on proton transport, free volume and pore size. The free volume is calculated by

Table 1
Diffusion coefficients of hydronium ion (D_H) and sulfonate group (D_S).

Membrane	$D_H \times 10^2 / \text{nm}^2 \cdot \text{ns}^{-1}$	$D_S \times 10^2 / \text{nm}^2 \cdot \text{ns}^{-1}$
Nafion	29.23	0.07
P21SA	20.72	0.10
SPEEK	5.18	0.35

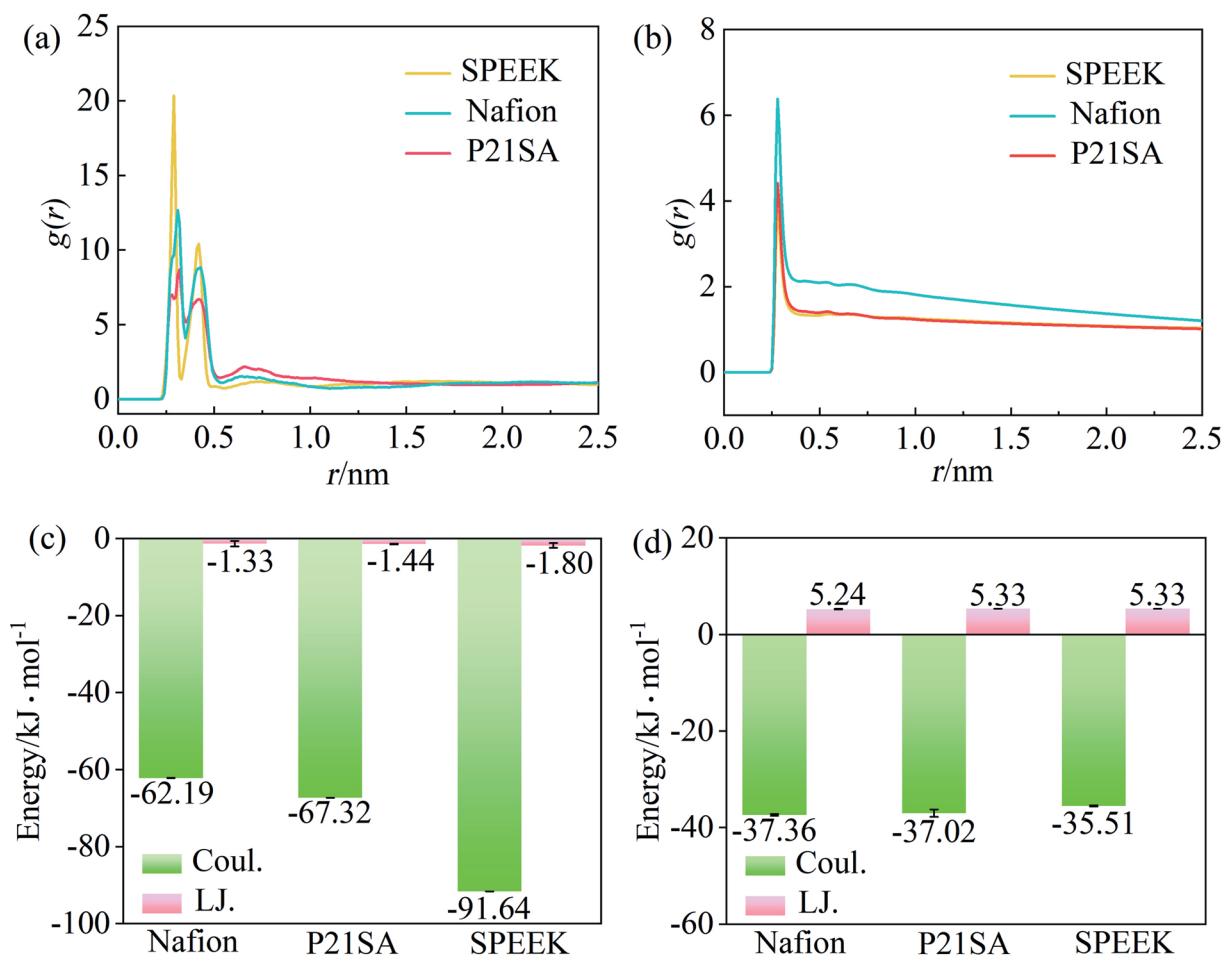


Fig. 3. Radial distribution functions for (a) $\text{SO}_3^- - \text{H}_3\text{O}^+$ and (b) $\text{H}_2\text{O} - \text{H}_2\text{O}$ for Nafion, P21SA and SPEEK. The interaction energy for (c) $\text{SO}_3^- - \text{H}_3\text{O}^+$ and (d) $\text{H}_2\text{O} - \text{H}_2\text{O}$ for Nafion, P21SA and SPEEK.

the probe-method, while the pore size is analyzed by Zeo++ [70]. The free volume snapshots are analyzed by the Multiwfn software [71,72]. At specific position, the distances between the probe and all of the atoms are calculated at first. If one of the distances is less than the sum of probe radius and atom radius, the volume is identified as non-free. Otherwise, it is defined as the free volume. The probe radius is set at zero in this work. Fig. S3 presents the spatial distribution of free volume in the membranes, with the blue regions indicating the free space. Quantitative analysis reveals that Nafion exhibits the most extensive free volume, indicating a more open and less densely packed polymer network. This abundant free space promotes the formation of larger and more continuous water clusters, which implies the existence of strong HBNs in the CHMs. In contrast, SPEEK shows a significantly reduced free volume (roughly 15% to 20%). The dense polymer matrix limits the size of water cluster, thereby favoring a transport process governed mainly by the vehicle mechanism. P21SA has the intermediate free volumes, falling between the Nafion and SPEEK.

In addition to the free volume analysis, Fig. 4 shows the pore size distribution and the corresponding mean pore sizes for the three membranes. Nafion has a broad distribution of large pores, with an average pore size around 0.298 nm. Such pore sizes facilitate the formation and interconnection of water channels that support proton hopping via the CHM. In contrast, SPEEK exhibits a narrow pore size distribution. The mean pore size is about 0.25 nm, reflecting a more compact structure that restricts HBN

connectivity and impedes extensive formation of water cluster. P21SA shows intermediate behavior, with the average pore size falling between those of Nafion and SPEEK.

3.4. Hydrogen-bond network

To further investigate the proton transport mechanism, the lifetime and number of hydrogen bonds are calculated. The data are shown in Fig. 5. The lifetime of hydrogen bonds is calculated by

$$\tau_{\text{HB}} = \int_0^{\infty} C(\tau) d\tau \quad (2)$$

where $C(\tau)$ is the autocorrelation functions

$$C(\tau) = \langle s_i(t)s_i(t + \tau) \rangle \quad (3)$$

$s_i(t) = \{0, 1\}$ for hydrogen bond i at time t . $\langle \cdot \rangle$ denotes the ensemble average. Fig. 5(a) shows the autocorrelation functions, and Fig. 5(c) shows the average lifetimes. Fig. 5(b) shows the molar ratio distribution in terms of hydrogen bond number per water molecule, while Fig. 5(d) shows the average number of hydrogen bond per water molecule.

The key distinction between SPEEK and Nafion lies in their microstructure [63]. SPEEK exhibits weak hydrophilic/

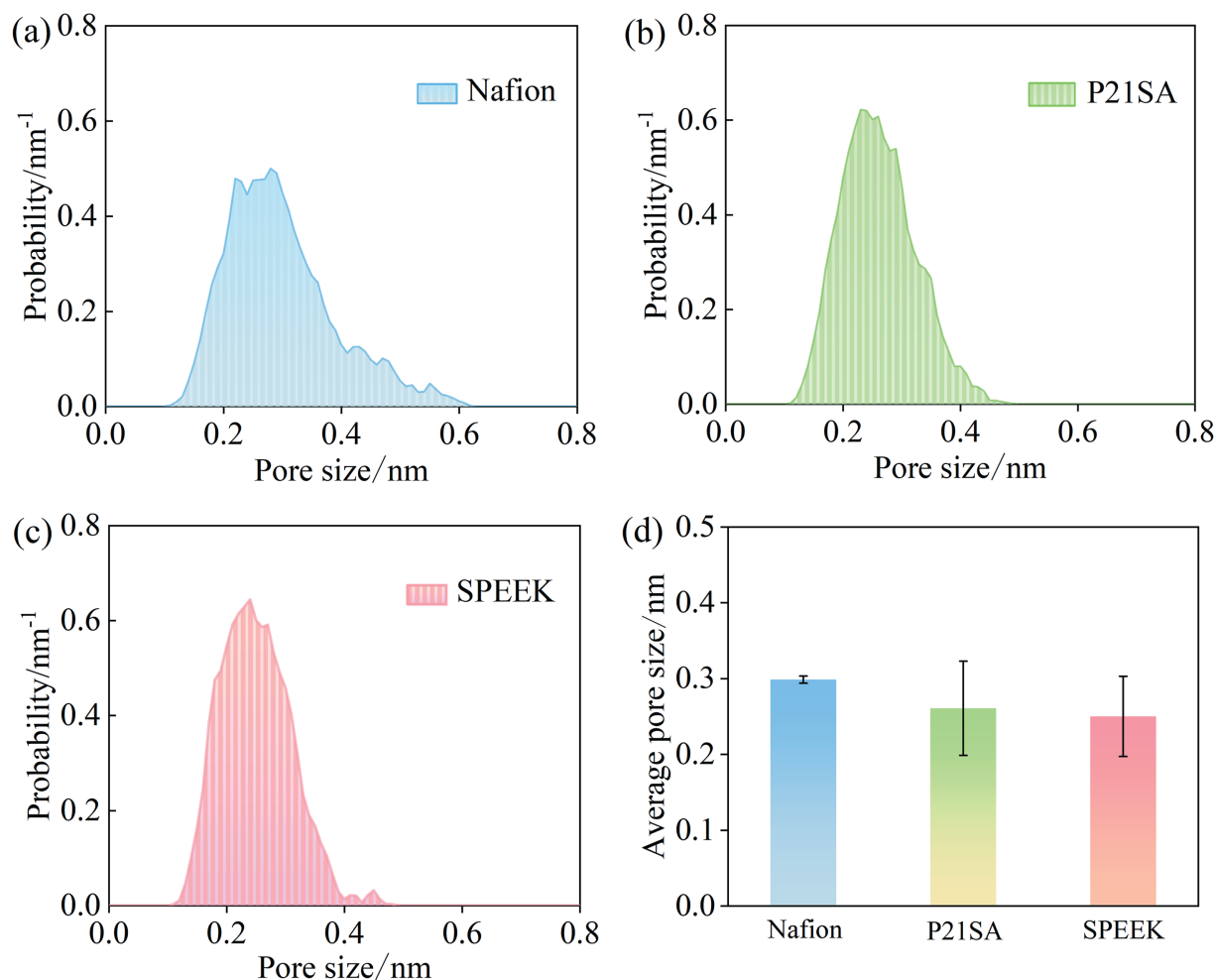


Fig. 4. (a–c) Probability distributions of pore size in Nafion, P21SA and SPEEK. (d) Average pore sizes for the three membranes.

hydrophobic interactions, which results in the formation of narrow and less interconnected channels within the membrane. The strong confinement significantly restricts the moving freedom of water molecules. Consequently, the hydrogen bonds in SPEEK show the longest lifetimes and the slowest HBN reorganization dynamics (*cf.* Fig. 5(a) and (c), and Table S6), which implies that the HBN is in a relative static state and the proton transport is dominated by the vehicle diffusion. In addition, water molecules in SPEEK have high probability to form hydrogen bonds with the number less than 2 (Fig. 5(b)). The membrane structure of SPEEK is rather rigid, which cannot effectively support the cooperative hydrogen-bond reorganization as in the CHM [73]. The proton transport is dominated by the vehicle mechanism, where the protons transport along the hydrated ions (H_3O^+ or H_5O_2^+).

In contrast, Nafion possesses a well-defined micro structure with wide and well-connected hydrophilic channels. This structure has great impact on the dynamic properties of hydrogen-bond network. As shown in Fig. 5(a) and (c), and Table S6, the hydrogen bonds in Nafion exhibit the shortest lifetimes and the highest HBN reorganization dynamics, which indicates the proton transport is dominated by the CHM. This behavior is in consistent with the high probability of one water molecule to form three and four hydrogen bonds; *cf.* Fig. 5(b). This is the direct evidence of forming a complete tetrahedral hydrogen-bond network in Nafion, which provides an ideal platform for efficient proton transport *via* the

CHM. For P21SA, the hydrogen-bond lifetime is between Nafion and SPEEK, indicating a hybrid mechanism of CHM and vehicle. In addition, the hydrogen-bond number distribution also exhibits the same hybrid behavior.

3.5. Water channel analysis

The water cluster is an important factor in determining the proton transport, which provides further insight into the transport mechanism of protons. Fig. 6(a) shows the schematics for the definition of water cluster. A water molecule is defined in the cluster, when the closest distance between the molecule and the other molecules in the cluster is less than 0.35 nm, which is also the distance to form hydrogen bonds.

Fig. 6(b) shows the time evolution for the ratio N_{max}/N , where N_{max} is the number of molecules in the largest cluster and N is the total number of water molecules. Nafion and P21SA exhibit relatively high and stable ratios, indicating the presence of long-lived and connected water channels that ensure continuous connectivity. In contrast, the ratio for SPEEK is lower, suggesting a more dispersed and less-connected water channel.

Fig. 6(c) shows the data of $R_g/\bar{L}$, where R_g is the average radius of gyration for the water clusters, and $\bar{L}$ is the average value of maximal distance between any two molecules in one cluster. $R_g/\bar{L}$

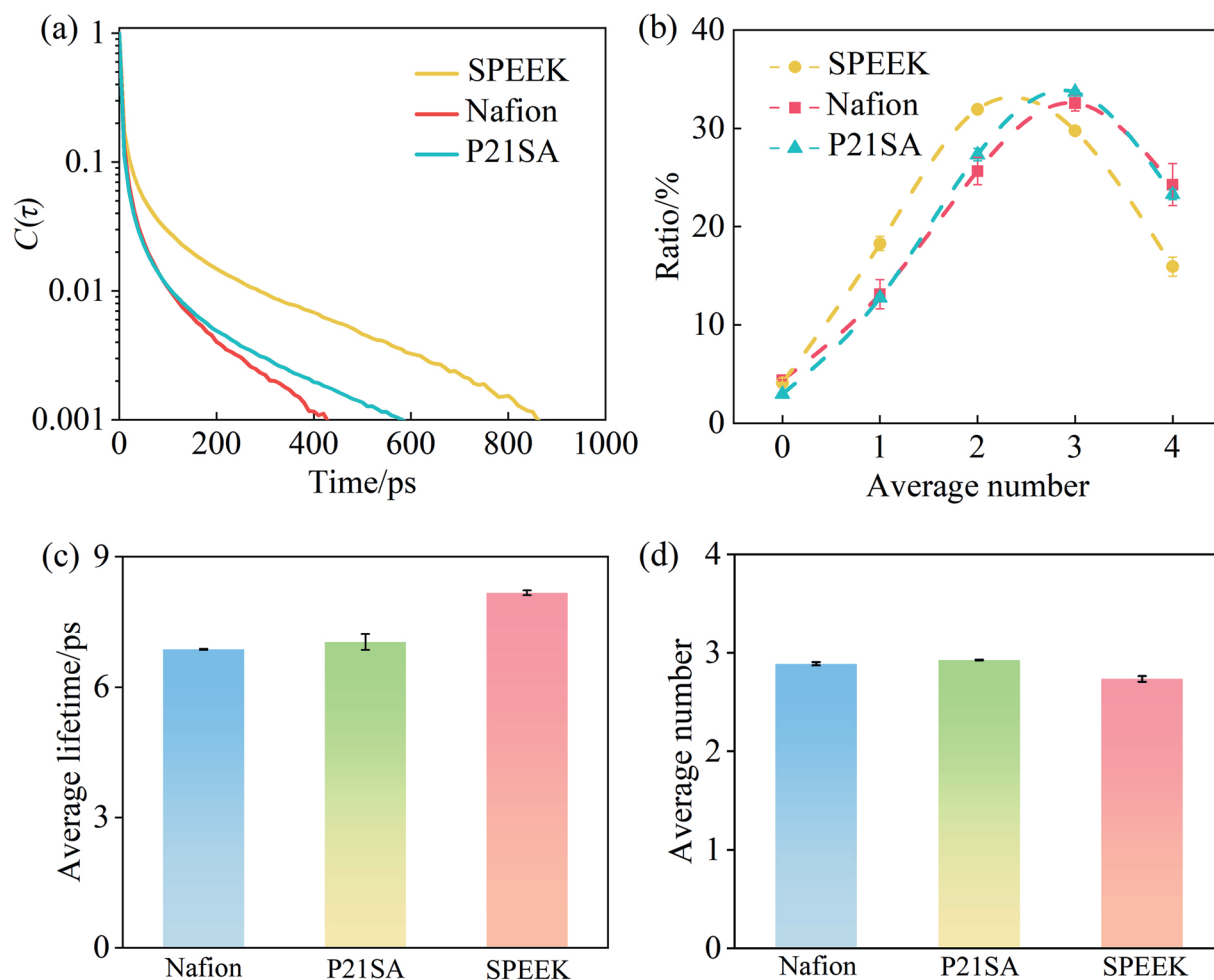


Fig. 5. (a) Auto-correlation function of hydrogen bond lifetime. (b) Molar ratio distribution in terms of hydrogen bond number per water molecule. (c) Average lifetime of hydrogen bonds. (d) Average number of Hydrogen bond number per water molecule.

describes the clusters' compactness and shape tortuosity in terms of their spatial distribution. Results shows that SPEEK exhibits high tortuosity (Fig. 6(c)), indicating more convoluted hydrated channels and long transport pathway for protons, which is unfavorable for rapid proton transportation. In contrast, Nafion has a relatively low-tortuosity, implying more connected channels that facilitate long-range proton transport.

Above results correlate well with R_g of the sulfonate groups shown in Fig. 6(d). The high- R_g in Nafion suggests more extended and flexible side chains, which promotes the formation of an extensive and overlapping network of sulfonate groups within the membrane's hydrophilic region. This creates an optimal pathway for protons to jump along the sulfonate groups [74]. Conversely, the much smaller R_g in SPEEK indicates more densely packed and restricted sulfonate groups, resulting in insufficient overlap between adjacent potential wells and thereby inhibiting proton hopping. Under these conditions, proton migration relies more heavily on the overall diffusion. The water channel structure can be observed from the snapshots of water cluster; see Fig. S4. The water clusters in Nafion exhibits an extensive network. The proton transport in Nafion prefers the CHM because of the sulfonate

group effects. In contrast, the water clusters in SPEEK have an incomplete network with many isolated structure, which implies that the proton transport rely more on the vehicle mechanism. For P21SA, the water clusters exhibit a hybrid state. These features can also be confirmed by the data of average cluster size (Fig. 6(e)) and the cluster-size distribution (Fig. 6(f)).

Hydration number is an important factor to influence the proton transport. With decreasing λ , the properties of confined water in PEMs deviate increasingly from those of bulk water [75]. As a result, the proton dissociation and transport dynamics are changed. However, the extent of this shift is membrane-dependent due to the differences of intrinsic structure. In particular, it is expected that the water channels in SPEEK would be disrupted at low λ . As a result, the hopping mechanism is restricted and the vehicle mechanism become dominant. In contrast, the proton transport in Nafion is weakly influenced by the hydration number, because of the appearance of well-connected and hydrophilic domain. The hopping mechanism in Nafion can persist over a wide range of hydration number [63]. As decreasing λ , the proton transport in P21SA should still exhibit the intermediate behavior between Nafion and SPEEK.

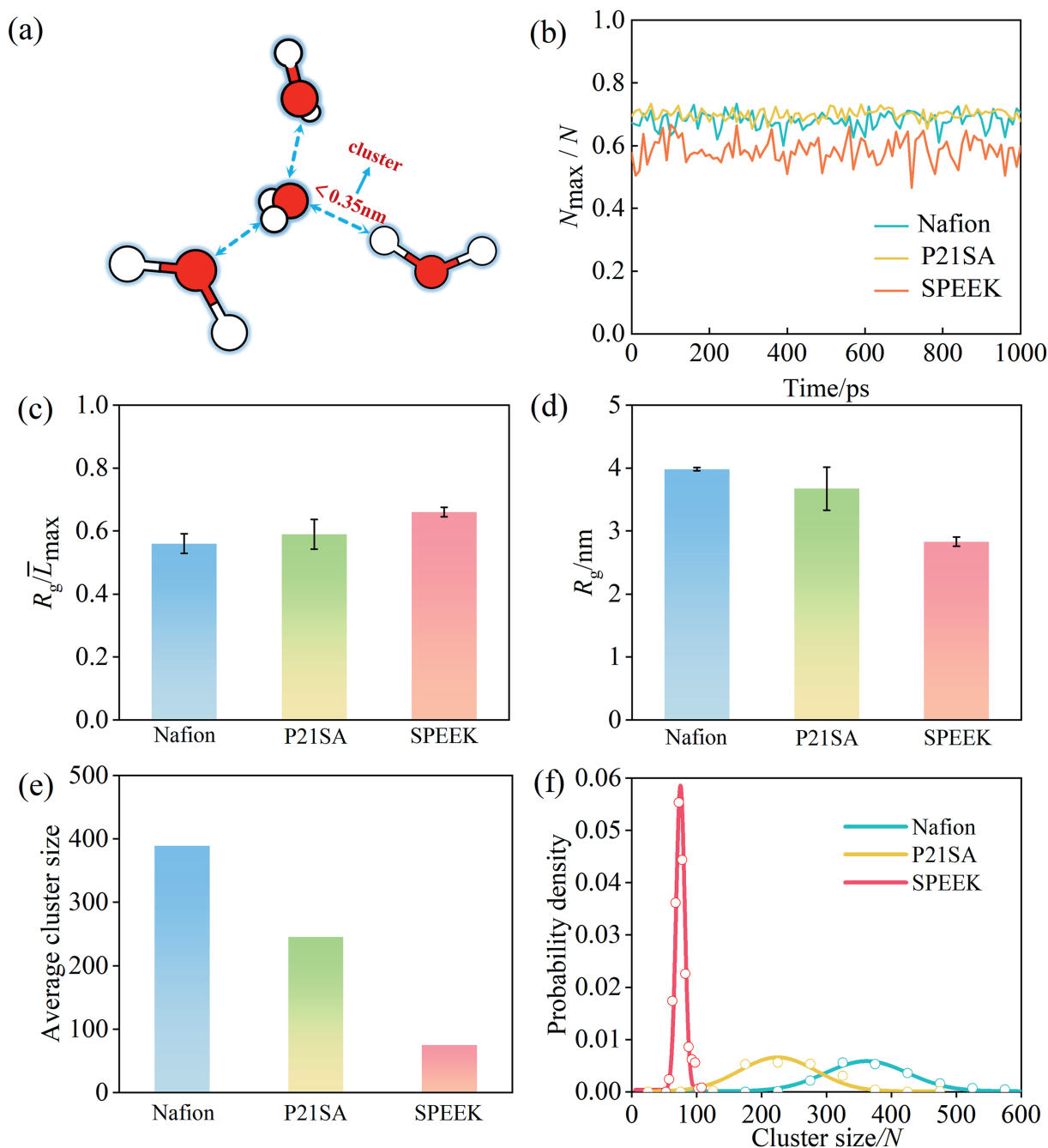


Fig. 6. (a) Schematics for the definition of water clusters. (b) Time evolution for the ratios of number of water molecules in the maximum cluster over the total number of molecules. (c) The shape index for water clusters, where R_g is the average radius of gyration for the water clusters, and $\bar{L}$ is the average value of maximal distance between any two water molecules in one cluster. (d) Radius of gyration of sulfonated groups. (e) Average size of water cluster (number of molecules). (f) Probability distribution of cluster size.

4. Conclusions

In this study, molecular dynamics simulations are conducted to elucidate the proton transport mechanisms in Nafion, P21SA, and SPEEK membranes by correlating the microstructure with dynamic transport properties. The structural differences fundamentally originate from the chemical composition of the polymers. The superior proton conductivity of Nafion originates from the flexible and hydrophobic perfluorinated backbone, which promotes the formation of wide and continuous hydrophilic nanochannels. These ionic nanochannels can be further optimized through the *in*

situ incorporation of nanofillers, which introduce additional functional sites to enhance the proton transport pathways [76]. In contrast, the aromatic backbone of SPEEK leads to a densely-packed matrix with narrow and poorly-connected nanochannels. The proton transport in SPEEK is dominated by the vehicle mechanism. P21SA exhibits intermediate properties between these two limiting cases. The aliphatic polyethylene backbone provides moderate flexibility, enabling partially connected water channels while maintaining a certain degree of confinement. Consequently, P21SA shows intermediate hydrogen-bond lifetimes and water coordination environments.

It is important to design hoping-dominated HBN with well-connected and wide-hydrated nanochannels, which are the essential factors for promoting the proton transportation. At the same time, the balance between ion mobility and channel confinement also plays a critical role, because unbalance effect may suppress the hydrogen-bond dynamics and can shift the proton transport toward to the vehicle mechanism. These results provide useful insights from molecular scale to understand the proton transport in proton exchange membrane.

CRedit Authorship Contribution Statement

Siyu Gong: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation. Ruifang Shi: Software, Investigation. Xuan Wang: Writing – review & editing, Software, Investigation. Xiaofei Xu: Writing – review & editing, Writing – original draft, Supervision. Qingwei Gao: Writing – review & editing, Writing – original draft, Supervision, Software, Resources. Shuangliang Zhao: Writing – review & editing, Writing – original draft, Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2026.03.005>.

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