Trifluoromethanesulfonimide-Based Hygroscopic Semi-Interpenetrating Polymer Network for Enhanced Proton Conductivity of Nafion-Based Proton Exchange Membranes at Low Humidity

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ABSTRACT

In this study, a super acid with impressive hygroscopicity, 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethanesulfonyl)imide (MPTI), is exploited to improve the proton conductivity of PEMs at low humidity. Importantly, MPTI can deliquesce into an aqueous solution by capturing moisture from air at a considerable rate. Investigation of the hygroscopicity of MPTI and the corresponding mechanism by molecular dynamics simulation show a total interaction energy between MPTI and water of $-368.13 \text{ kJ mol}^{-1}$, which greatly exceeds those of model derivatives with other typical hygroscopic groups. To apply MPTI in PEMs and prevent leakage, MPTI is incorporated into a semi-interpenetrating polymer network via *in situ* polymerization, and Nafion-based composite membranes are fabricated. The water uptake of the obtained hybrid membranes is substantially increased by up to 66.61% at 40% RH and 90.04% at 95% RH. This optimization of the water environment facilitates the dissociation of protons and the formation of hydrogen bond networks for high-speed proton conduction. As a result, the proton conductivity of the membranes increases by up to two orders of magnitude at low humidity. Notably, this composite membrane enhanced the performance of a single fuel cell at 60% RH by 41.9%.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising energy conversion devices owing to their advantageous features such as high efficiency, eco-friendliness, and rapid startup.[1-4] As the core component of PEMFCs, proton exchange membranes (PEMs) act as both a proton conductor and a fuel/oxidizer separator.[5-7] Water plays a vital role in the proton conduction process in PEMs.[8] On one hand, PEMs possess microphase separation structures, in which side chains with terminal sulfonic acid groups form hydrophilic phases and the polymeric backbones form hydrophobic phases.[9, 10] In the hydrophilic phases, water facilitates the dissociation of acid groups and swelling to form well-connected ionic channels.[11-14] On the other hand, to realize proton diffusion, water acts as an ion carrier by forming H_9O_4^+ (Eigen cation) or H_5O_2^+ (Zundel cation) (vehicle mechanism) and as a conveyor for rapid delivery of protons by the continuous breaking and forming of hydrogen bonds (Grotthuss mechanism).[15, 16]

Typically, PEMFCs are expected to operate at high temperatures and low humidities to overcome the problems associated with low electrochemical reaction rates, catalyst poisoning, and complex water management systems.[11, 17-19] However, dehydration at high temperatures and low humidities results in dramatically decreased proton conductivity and poor fuel cell performance. Thus, there is a necessity to enhance the water-retention ability of PEMs at low relative humidity (RH).

Incorporating hygroscopic materials into PEMs is a suitable approach to address this issue.[1, 11, 15, 18, 20] Hygroscopic materials can hydrate PEMs by capturing the moisture in feed gases and retaining the water generated in electrode reactions. Great efforts have been devoted to exploiting high-performance hygroscopic materials, with typical materials including high

1 concentrations of sulfonated groups,[21] phosphoric acid groups,[1, 18] polyethylene glycol
2 (PEG) segments,[14, 17] *N*-heterocyclic groups,[15, 20] and Brønsted acids[22]. For example, a
3 composite membrane was fabricated by mixing PEG-modified graphene oxide with a Nafion
4 matrix. Hydrogen bonding between the ethylene oxide groups and water molecules allowed
5 retention of water to form hydration layers at the filler surfaces, which facilitated ionic conduction
6 at low humidity.[17] Furthermore, loading of phytic acid onto MIL101 (a metal–organic
7 framework) and incorporation into a Nafion membrane increased the proton conductivity at low
8 humidity by several orders of magnitude.[1] Thus, high-performance hygroscopic materials can
9 be exploited to improve the proton conductivity of PEMs at low humidity.

10 Trifluoromethanesulfonimide (triflimidic acid, HNTf_2 , $\text{CF}_3\text{SO}_2\text{-N}^+\text{H-SO}_2\text{CF}_3$) is a crystalline
11 solid with incredible hygroscopicity, which can easily deliquesce into an aqueous solution by
12 capturing moisture when exposed to air.[23, 24] In addition, HNTf_2 is one of the strongest acids
13 (even stronger than trifluoromethanesulfonic acid, $\text{CF}_3\text{SO}_2\text{OH}$).[23-25] Incorporation of the super
14 acid HNTf_2 into a PEM could significantly increase proton concentrations in the ionic channels
15 and optimize the chemical environment to further enhance proton conduction. Thus, the
16 incorporation of HNTf_2 is expected to improve the performance of PEMs significantly at low
17 humidity. However, to avoid undesirable leakage from PEMs, HNTf_2 should be immobilized on
18 an insoluble support. Although numerous materials have been exploited as supports for
19 immobilization of hygroscopic groups,[26-30] incorporation of these supports (proton-insulated
20 bulk materials) tends to render tortuous ionic channels as well as decrease the available space for
21 proton conduction.[17, 31]

22 Semi-interpenetrating polymer networks (SIPNs), composite polymers consisting of a linear
23 polymer entrapped within a polymer network, have been exploited as ion exchange membranes

for fuel cells over the last few decades.[32-34] By incorporating desirable monomers into the linear PEM matrix, an *in situ* polymerization reaction can be performed to form a cross-linked polymer network, thus obtaining an SIPN. The polymer network can act as an excellent support for hygroscopic groups, which can be facilely grafted onto the polymer network by rationally designing the monomer. The insolubility of the cross-linking polymer network can significantly inhibit leaching of the hygroscopic groups. Moreover, the open structure of the polymer network without tortuosity promotes protons shuttling, which can be tuned by microphase separation in the PEM to further facilitate proton conduction.[35]

Herein, to realize PEMs with improved proton conductivity, we designed a hygroscopic monomer by linking HNTf₂ with propyl methacrylate to form 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethanesulfonyl)imide (MPTI). To quantify the hygroscopicity of MPTI, the interaction energy between water and MPTI was calculated using a molecular dynamics simulation (MDS). SIPNs were fabricated by blending Nafion and polymeric MPTI. Nafion was employed as the linear polymer because it is a state-of-the-art polyelectrolyte for PEMs. The performance of the obtained composites as PEMs was thoroughly investigated, especially in regards to water uptake and proton conductivity at low humidity.

2. Experimental Section

2.1 Materials. Nafion 2021 solution (20 wt.%) was purchased from DuPont Co. Ltd. Trifluoromethyl sulfonamide (95%) were purchased from Tianjin Heowns Biochemical Technology Co. Ltd. Potassium sulfopropyl methacrylate (SPMA-Na, 98%), thionyl chloride (99.5%), triethylamine (99.5%), propylene carbonate (PC, anhydrous, 99.9%), dimethylformamide (DMF, anhydrous, 99.8%), 1,2-dichloroethane (anhydrous, 99.5%),

tetrahydrofuran (THF, anhydrous, 99.5%), azodiisobutyronitrile (AIBN, recrystallized, 99.9%), ethylene glycol dimethacrylate (EGDMA, $M_w \approx 750$), and lithium hydride (97%) were purchased from Shanghai Macklin Biochemical Co. Ltd. Before use, the polymerization inhibitors in EGDMA were removed using a silica column. All other reagents were used directly without further purification. Deionized water was utilized in all experiments.

2.2 Synthesis of Lithium 1-[3-(Methacryloyloxy)propylsulfonyl]-1-(trifluoromethanesulfonyl)imide. The synthesis procedure for 1-(sulfonyl chloride)-propyl methacrylate is summarized in Scheme 1. THF (50 mL) was loaded in a flask, and freshly dried SPMA-Na (30.0 g) was dispersed in THF under mechanical stirring in an Ar atmosphere. DMF (3.4 mL) was carefully injected into the flask as a catalyst. After cooling the flask to 0 °C, thionyl chloride (39.9 g) was added dropwise. Caution must be taken because thionyl chloride is highly poisonous and corrosive. The reaction was allowed to proceed at 0 °C for 1 h and then at 30 °C for 12 h. The obtained transparent solution was slowly poured into an ice slurry (~200 mL). The organic phase was diluted with dichloromethane (160 mL) and then separated from the water phase using a separatory funnel. The obtained organic solution was washed with abundant water to remove the acid by-product and residual SPMA-Na, and then dried using $MgSO_4$. Subsequent evaporation gave a light-orange oil of 1-(sulfonyl chloride)-propyl methacrylate.

Scheme 1. Synthesis of 1-(Sulfonyl chloride)-propyl Methacrylate.

The synthesis procedure for triethylammonium MPTI is summarized in [Scheme 2](#). 1-(Sulfonyl chloride)-propyl methacrylate (22.2 g) was dissolved in THF (30 mL), and the resulting solution was cooled to 0 °C (solution A). Trifluoromethyl sulfonamide (14.6 g) and triethylamine (21.8 g) were dissolved in THF (40 mL), and the resulting solution was cooled to 0 °C (solution B). Subsequently, using a dropping funnel, solution A was added dropwise into solution B under stirring in an Ar atmosphere. The mixture was kept at 0 °C for 1 h and then at 30 °C for 2 h. The liquid was separated from the mixture by filtration and concentrated using a rotary evaporator to obtain a light-orange oil. The oil was diluted with dichloromethane (80 mL) and washed with water. The water phase was removed using a separatory funnel and MgSO₄ was added to further dry the organic phase. A catalytic amount (~0.2%) of 4-methoxyphenol was added as an antioxidant. The organic phase was then evaporated to obtain a light-orange oil of triethylammonium MPTI.

Scheme 2. Synthesis of Triethylammonium MPTI.

The synthesis procedure for lithium MPTI is summarized in [Scheme 3](#). Triethylammonium MPTI (60.0 g) was dissolved in THF (90 mL) under an Ar atmosphere. Then, lithium hydride (2.6 g) was

carefully and slowly added into the solution. After the obtained suspension was stirred at 30 °C for 12 h, residual lithium hydride was removed by skimming. Then, the solution was concentrated using a rotary evaporator and dried at 25 °C under vacuum to obtain a yellowish gel. The gel was cooled to -20 °C and crystallized in anhydrous dichloromethane to obtain a white powder of lithium MPTI.[36]

Scheme 3. Synthesis of Lithium MPTI.

2.3 Fabrication of Composite Membranes. The fabrication process for the Nafion-based composite membranes is summarized in [Scheme 4](#). Nafion 2021 solution (1.0 g) was diluted using DMF (1.0 mL) and PC (1.0 mL). Then, lithium MPTI (x g, $x = 0.006, 0.012$ or 0.018 in this study), EGDMA ($0.5x$ g), and AIBN ($0.08x$ g) were added. The mixture was stirred at 25 °C for 12 h to obtain a homogeneous solution and then degassed by ultrasonication. Finally, the solution was cast onto a PTFE plate, dried at 60 °C for 24 h, and annealed at 140 °C for 2 h. The resulting membrane was peeled off the plate, immersed in 2 M H_2SO_4 at 60 °C for 24 h to realize ion exchange (from Li^+ to H^+ , generating MPTI acid), and washed with abundant water to remove residual H_2SO_4 . The

membranes were designated as Nafion/MPTI-X, where X is the weight ratio between MPTI and

Nafion during the membrane fabrication process ($X = \frac{x}{20 \text{ wt.}\% \times 1.0 \text{ g}}$).

Scheme 4. Fabrication of Nafion/MPTI-X composite membranes.

2.4 Characterization. The *in situ* fabrication of a SIPN was confirmed using nuclear magnetic resonance (NMR) spectroscopy. For NMR experiments, soluble samples were dissolved in DMSO-*d*₆ and spectra were recorded on a Varian INOVA spectrometer (600 MHz). Insoluble samples were crumbled in liquid nitrogen and spectra were recorded on a Jeol JNM-ECZ600R spectrometer using the CPMAS method (150 MHz for ¹³C and 600 MHz for ¹H).

Morphology of membranes was observed using field emission scanning electron microscope (FESEM, S-4800, Hitachi Ltd., Japan). The sample was broken in liquid nitrogen, and Au was sprayed at the surface of cross section.

The microphase separation of membranes was observed using high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). The samples were immersed in 1 M aqueous AgNO₃

for 24 h, immersed in water for 3 days (replaced water every half day), and then dried under vacuum until constant weight, successively. Sulfonic acid groups ($-\text{SO}_3^-\text{H}^+$) and trifluoromethyl sulfonamide groups ($-\text{SO}_2-\text{NH}^+-\text{SO}_3-\text{CF}_3$) can be stained by Ag^+ in this process. The sample was processed to ultramicrocut with uniform thickness of 70 nm, and loaded on a copper grid.

2.5 Molecular Dynamics Simulation of Hygroscopicity. All the MD simulations were carried out using the GROMACS 5.1.4 software package with GROMOS96-54a7 all atom force field. This force field has been widely used for simulations [37, 38]. Moreover, the optimized geometry and topology files of all the molecules were generated by Automated Topology Builder (ATB) of Repository Version 2.2 [39], while the atomic charges were calculated by DFT method with B3LYB/6-31G*. The SPC water model was applied as solvent. The force field functions met with the Lennard-Jones potential with geometric averages combination rules as well as the Columbic potential was used for non-bonded calculation.

In the MD simulations, the simulation box size $4\times 4\times 4\text{ nm}^3$ was built. The simulation processes were almost the same as used in previous paper with periodic conditions in *xyz* directions [37, 38]. In brief, energy minimization was performed by the steepest descent method in canonical (NVT) ensembles, and followed by the conjugate gradient method for further eliminating the steric clashes and inappropriate geometry. The MD simulations were then performed in NPT ensembles at 298 K using a V-rescale thermostat coupling algorithm. During both the equilibration and production MD simulations, leapfrog Verlet algorithm with a time step of 2 fs was used for integration of the trajectories. The LINCS algorithm was used for all h-bonds, and the cutoff distance of the neighbor list was set at 1.2 nm. The cutoff distance of 1.4 nm was adopted to calculate the L-J potential and electrostatic interactions using particle mesh Ewald (PME) summation method. The initial atomic

velocities of the system were generated by Maxwell–Boltzmann distribution at the specified temperature of 298 K.

2.6 Water Uptake and Area Swelling of Membranes. Each membrane sample was fully dried at 60 °C under vacuum, and the initial weight (m_0), thickness (h_0) and area (A_0) were measured. Then, the membrane sample was placed in a temperature–humidity chamber at 60 °C for 12 h. The resulting weight (m_1), thickness (h_1) and area (A_1) were measured. The water uptake, area swelling and thickness swelling of membranes were calculated using equations 1, 2 and 3, respectively.

$$\text{Water uptake} = \frac{m_1 - m_0}{m_0} \quad (1)$$

$$\text{Area swelling} = \frac{A_1 - A_0}{A_0} \quad (2)$$

$$\text{Thickness swelling} = \frac{h_1 - h_0}{h_0} \quad (3)$$

2.7 Proton Conductivity. The proton conductivity (in-plane) of each membrane sample was determined using electrochemical impedance spectroscopy with instrument (Princeton PARSTAT 2273). The membrane holder was fabricated by fixing two parallel platinum wires (diameter = 0.5 mm) at a hollow-out PTFE plate. The distance of platinum wires was 1.5 cm. Another hollow-out PTFE plate was employed as cover plate to fix the membrane sample. Before testing, the membrane was cut into ca. 2.0×0.5 cm² square, and sandwiched by the membrane holder and the cover plate. Then, this system was exposed to a certain temperature and a certain humidity for 12 h. Finally, the electrochemical impedance spectrum was measured over the frequency range of 1 MHz to 1 Hz. The proton conductivity (σ , mS cm⁻¹) of the membrane sample was calculated using equation 4, where l (cm) is the distance between the parallel platinum wires, a (cm) is the breadth

of the membrane samples, b (cm) is the thickness of the sample, and R (k Ω) is the resistance of the membrane sample obtained from the electrochemical impedance spectrum. Three parallel tests were carried out for each sample, and the error range should be no more than 2.0%.

$$\sigma = \frac{l}{abR} \quad (4)$$

The activation energy (Ea , kJ mol⁻¹) for proton conduction in the membrane was employed to investigate the ion-transfer resistance, which was obtained based on the Arrhenius equation. An Arrhenius plot was constructed with the Napierian logarithm of the proton conductivity on the Y-axis and the reciprocal value of the temperature in Kelvin on the X-axis. The slope of the curve was designated as k and the activation energy was calculated using equation 5. R in equation 5 is 8.3145 J·K⁻¹·mol⁻¹.

$$Ea = -Rk \quad (5)$$

2.8 Single Fuel Cell Test. After wetting the catalyst (Pt/C, 60%, Johnson Matthey) with water, Nafion 2021 and isopropanol was added. The mixture was stirred for 1 h and then ultrasonicated for 30 min to obtain a catalyst slurry. The slurry was coated on the surface of carbon papers using silk-screen printing, with loadings of 0.1 mg cm⁻² for the anode and 0.25 mg cm⁻² for the cathode. The membrane sample was sandwiched between the two electrodes and hot-pressed at 130 °C and 1000 kg fcm⁻² for 10 min to obtain a membrane electrode assembly (MEA). The MEA was tested in a fuel cell device at 60 °C with O₂ and H₂ flow rates of 200 and 150 mL min⁻¹, respectively. The backpressure was 0.1 MPa.

3. Results and Discussion

3.1 Hygroscopicity of MPTI. To demonstrate the superior hygroscopicity of MPTI, a water uptake experiment was carried out. MPTI was kept under 40% RH at 30 °C, and the weight was measured at set time intervals. Typical highly hygroscopic materials, including concentrated sulfuric acid, concentrated phosphoric acid, and PEG, were employed as references. As shown in [Figure 1a](#), compared with the references, MPTI can capture far more moisture from air. In addition, the sharp slope of the water uptake curve indicates that MPTI can capture moisture at a considerable rate, which is very important for the rapid hydration of PEMs operated under harsh conditions. The images in [Figure S1](#) visually show the superior hygroscopicity of MPTI. Pristine MPTI, a white crystalline powder, easily deliquesces into an aqueous solution after 12 h by capturing moisture in air.

Figure 1. Water uptake of materials kept under 40% RH at 30 °C.

A MDS was employed to further demonstrate the superior hygroscopicity of MPTI and to investigate the hygroscopic mechanism. Model derivatives with typical hydrophilic groups were employed as references. The structures of the model molecules and the simulation results are shown in [Figure 2](#). The total interaction energy between MPTI and water ($-368.13 \text{ kJ mol}^{-1}$) is

considerably higher than the energies of derivatives modified with a sulfonated group ($-201.76 \text{ kJ mol}^{-1}$), phosphonic acid ($-245.93 \text{ kJ mol}^{-1}$), imidazole ($-188.21 \text{ kJ mol}^{-1}$), and ethylene glycol ($-187.24 \text{ kJ mol}^{-1}$), implying that MPTI has superior hygroscopicity. A detailed analysis of the interaction energies (Figure 2a) indicates that the high total interaction energy between MPTI and water mainly originates from coulombic interactions ($-292.3 \text{ kJ mol}^{-1}$). The perfluorosulfonic and sulfonyl groups of MPTI immensely decrease the density of the nitrogen-atom electron cloud, which dramatically increases the dipole of MPTI, resulting in strong coulombic interactions. In addition, analysis of the average number of hydrogen bonds (Figure 2b) further reveals MPTI to have superior hygroscopicity. Owing to its strong attraction to water molecule, the average number of hydrogen bonds for MPTI is as high as 10.517, which is $\sim 2\text{--}3$ fold the values for the model molecules.

Figure 2. MDS results: (a) interactions between water molecules and model molecules and (b) average number of hydrogen bonds for model molecules.

3.2 Synthesis of MPTI and Nafion/MPTI-X. The successful synthesis of MPTI was confirmed using ^1H , ^{13}C , ^{19}F , and ^3Li NMR spectroscopy, as shown in Figure 3a–3d. In the ^1H NMR spectrum (Figure 3a), the single peaks at 6.035 and 5.671 ppm correspond to the hydrogen atoms of the terminal alkenyl group. The single peak at 1.888 ppm corresponds to the hydrogen atom of the methyl group. The triplet peaks at 4.182 and 3.071 ppm correspond to the hydrogen atoms at location no. 6 and location no. 4, respectively. The quintet peak at 2.029 ppm corresponds to the hydrogen at location no. 5.[40, 41] The area ratio of the peaks, which is shown below the spectrum, closely matches the atom ratio of the MPTI chemical formula. The ^{13}C NMR spectrum in Figure 3b exhibits a typical quartet peak at ~ 120 ppm, which is a signature of the carbon atom in a trifluoromethyl group. The peak at 52.2 ppm corresponds to the carbon linked to the trifluoromethanesulfonimide group. The other carbon atoms indicated by peaks in the ^{13}C NMR spectrum also agree well with the MPTI chemical formula.[41] In addition, the ^{19}F and ^3Li NMR spectra in Figure 3c and 3d indicate the presence of a Li atom and a F atom. These results verify that MPTI was successfully synthesized.

Figure 3. (a) ^1H NMR, (b) ^{13}C NMR, (c) ^{19}F NMR, and (d) ^7Li NMR spectra of MPTI in DMSO- d_6 .

The formation of SIPNs by *in situ* polymerization in the Nafion/MPTI-X membranes was confirmed using solid-state ^1H and ^{13}C NMR spectroscopy, as shown in Figure 4. The peaks at 6.035 and 5.671 ppm in the ^1H NMR spectrum correspond to the hydrogen atoms of the vinyl groups of MPTI and EGDMA (Figure 4a), and the peaks at 136.3 and 126.0 ppm in the ^{13}C NMR spectrum correspond to the carbon atoms of the vinyl groups of MPTI and EGDMA (Figure 4b). After thermal treatment, these four peaks disappear completely. In the ^1H NMR spectrum, a series of new peaks appear at ~ 2.0 ppm, corresponding to the hydrogen atoms of the straight-chain alkane formed by addition polymerization of the vinyl groups. A series of new peaks appear at ~ 21.0 ppm

in the ^{13}C NMR spectrum, corresponding to the carbon atoms of the straight-chain paraffin formed by addition polymerization of the vinyl groups. In addition, the results of NMR also fully agreed with the results of Fourier Transform Infrared Spectrometry (FT-IR, Figure S2) and X-ray photoelectron spectroscopy (XPS, Figure S3). In this case, the *in situ* polymerization was proved to be successfully proceeded.

Figure 4. Solid-state (a) ^1H NMR and (b) ^{13}C NMR spectra of the Nafion/MPTI-9 membrane. The corresponding spectra of EGDMA and MPTI are shown for reference.

3.3 Morphology and microphase separation of membrane. The SEM images of the membrane cross sections (Figure 5a–h) indicate that the hybrid membranes are very homogeneous and dense without any defects. The well dispersion of MPTI in the composite membrane can be exhibited by the EDX-mapping of nitrogen element, as shown in Figure S4. The microphase separation structures of the Nafion-based membranes were observed using HRTEM. The hydrophilic phases possessing negatively charged groups (sulfonated groups, trifluorosulfimide groups, etc.) can be stained using Ag^+ , but the hydrophobic phases consisting of nonpolar and crystalline polymer chains cannot. Ag is a heavy metal which can effectively shield the work electron of TEM, resulting in black regions in the images. Thus, the black regions in Figure 5i–l

correspond to the stained hydrophilic phases, whereas the bright regions are the stain-free hydrophobic phases. The Nafion membrane exhibits a well-defined microphase separation structure with clear hydrophilic/hydrophobic boundaries. The widths of hydrophilic ionomer domains can be directly measured in the images. However, the hydrophilic phases are narrow with widths of 3.1-3.6 nm. After incorporating the MPTI semi-interpenetrating polymer network, a well-defined microphase separation structure with clear hydrophilic/hydrophobic boundaries is still observed. However, the hydrophilic ionomer domains of Nafion/MPTI-9 are broadened to 3.8–5.1 nm. This impressive broadening of the hydrophilic ionomer domains can provide unrestricted and well-defined ionic pathways for proton conduction.

Figure 5. SEM images of membrane cross sections: (a, b) Nafion, (c, d) Nafion/MPTI-3, (e, f) Nafion/MPTI-6, and (g, h) Nafion/MPTI-9; TEM images of (i, j) Nafion and (k, l) Nafion/MPTI-9.

Small Angle X-ray Scattering (SAXS) of membranes was also employed to study the microphase separation structure of membranes, as shown in [Figure S5](#). Nafion showed a typical peak at $q=1.86 \text{ nm}^{-1}$ (q is the scattering vector), which indicated the distance of hydrophilic domains was 3.38nm. This value agreed with size measured from the TEM images. After incorporating MPTI, new peaks appeared at 1.21-1.39 nm^{-1} , indicating new hydrophilic domains with distance of 5.19 - 4.52 nm were formed. The density of new peaks was positively correlated to the incorporating amount. These results further verifying that the incorporation of MPTI induced the formation of broader hydrophilic ionomer domains.

3.4 Water Uptake, Area Swelling, and Hydration Numbers of Membranes. The water uptake and area swelling of the membranes in water were tested, as shown in [Figure 6](#). In general, incorporating a super-hygroscopic material into a membrane will significantly increase the osmotic pressure and water absorption, resulting in excessive swelling of the membrane and degradation of the mechanical strengthen.[42-44] However, incorporation of the MPTI SIPN into Nafion only increased the area swelling slightly from 22.32% (Nafion) to 28.46% (Nafion/MPTI-9) at 30 °C ([Figure 6a](#)). The thickness swelling shows similar tendency with the area swelling ([Figure 6b](#)). This phenomenon is attributed to the strong cross-linking interactions introduced by the MPTI SIPN into the hybrid membrane, which reinforces the polymer matrix and prevents it from collapsing in water. In this case, the mechanical properties of the membranes were largely preserved ([Figure S6](#)). Meanwhile, owing to the super hygroscopicity of the MPTI SIPN, the water uptake increased from 28.21% for Nafion to 36.86% for Nafion/MPTI-9 at 30 °C ([Figure 6c](#)). A large amount of water molecules in the membrane can greatly benefit proton conduction, as discussed in the Introduction.

Figure 6. (a) Area swelling, (b) Thickness swelling and (c) Water uptake of Nafion-based membranes in water.

Figure 7. (a) Water uptake and (b) hydration number of membranes at low RH and 60 °C.

The water uptake of the membranes under low RH conditions verify the superior water retention properties of the MPTI SIPN, as shown in Figure 7a. Owing to this superior deliquescence, incorporation of the MPTI SIPN significantly increases the water uptake of the hybrid membranes by up to 66.61% at 40% RH and 90.04% at 95% RH. Analysis of the hydration number (λ) reveals that the hybrid membranes capture numerous water molecules (Figure 7b), which can act as a solvent to facilitate the dissociation of protons and the formation of hydrogen bond networks for high-speed proton conduction.[17]

3.4 Proton Conductivity and Single Fuel Cell Performance of Nafion/MPTI-X Membranes.

Proton conductivity is a critical parameter for determining the performance of fuel cells.[1, 11, 15, 17] As shown in Figure 8a, the proton conductivity of the Nafion membrane is 71.8–206.9 mS cm⁻¹ at 20–90 °C and saturated humidity. Incorporating the MPTI SIPN significantly increases the proton conductivity to 107.2–256.4 mS cm⁻¹ at 20–90 °C and saturated humidity. Meanwhile, the activation energy of proton conduction decreases from 13.22 kJ mol⁻¹ for the Nafion membrane to 10.89 kJ mol⁻¹ for Nafion/MPTI-9 (Figure 8b). These results indicate that protons transfer through the composite membrane is more facile due to the introduction of low-energy-barrier pathways.[17, 45] This phenomenon is attributed to three factors: 1) the super acidity of MPTI significantly increases the local acid concentration in the ionic channels, optimizing the chemical environment for proton conduction; 2) incorporating the hydrophilic MPTI SIPN into the membrane increases the water uptake (Figure 6 and Figure 7), facilitating the dissociation of acid groups, which provides more protons as charge carriers, and the construction of hydrogen networks, which promotes high-speed proton conduction by the Grotthuss mechanism;[14, 46-50] and 3) the pendent HNTf₂ groups on the interconnected networks can act as proton carriers to further accelerate proton conduction, with optimization of the microphase separation structure

allowing the formation of unrestricted and well-defined ionic pathways for proton conduction (Figure 5j).[35]

To further evaluate the potential of the hybrid membranes for operation at low humidity, it is of significance to investigate the relationship between the proton conductivity of the membranes and RH, as shown in Figure 8c. The proton conductivity of the Nafion membrane sharply decreased from 189.1 mS cm⁻¹ at 100% RH to only 0.0488 mS cm⁻¹ at 10% RH. In sharp contrast, incorporating the MPTI SIPN dramatically increased the proton conductivity by up to two orders of magnitude at low humidity (229.67 mS cm⁻¹ at 100% RH and 1.66 mS cm⁻¹ at 10% RH). The impressive conductivity of the hybrid membrane is attributed to the super hygroscopicity of MPTI, which significantly increases the water uptake and hydration number, thus optimizing the water environment in the membrane for facile proton conduction. Moreover, the PEG segments in the EGDMA cross-linker are Lewis base sites and can act as proton acceptor sites to facilitate the dissociation and hopping of protons at low humidity.[17]

Single fuel cells were fabricated to evaluate the practical applicability of the hybrid membranes and to demonstrate the advantages of incorporating the highly hygroscopic MPTI SIPN. As shown in Figure 8d, the maximum power density of the cell equipped with the Nafion membrane is 157.51 mW cm⁻¹ at 60% RH and 60 °C. In sharp contrast, the maximum power density of the cell equipped with Nafion/MPTI-9 membrane is 223.60 mW cm⁻¹ under the same conditions (41.9% increase). This enhanced performance is a result of the impressive improvement of proton conductivity in the hybrid membrane, which reduces the resistance of proton transfer between the electrodes.

Figure 8. (a) Proton conductivity of Nafion-based membranes at different temperatures and saturated humidity, (b) activation energy of proton conduction in various membranes at saturated humidity, (c) proton conductivity of membranes at different humidities and 60 $^{\circ}\text{C}$, and (d) performance of single fuel cells equipped with various membranes at 60 $^{\circ}\text{C}$ and 60% RH.

4. Conclusion

In this study, MPTI was designed as a water molecule trap to improve the performance of PEMs at low humidity. Water uptake tests confirmed the impressive hygroscopicity of MPTI, with MPTI capturing considerably more moisture from air at a higher rate than many typical hygroscopic materials, such as sulfuric acid, phosphoric acid, and PEG. Furthermore, MPTI easily deliquesced

1 into an aqueous solution in air at low humidity. These features are very important for the rapid
2 hydration of PEMs operated under harsh conditions. A MDS confirmed the high hygroscopicity
3 of MPTI, with the total interaction energy between MPTI and water of $-368.13 \text{ kJ mol}^{-1}$, resulting
4 predominantly from coulombic interactions ($-292.3 \text{ kJ mol}^{-1}$), being much greater than that of
5 model derivatives with other typical hygroscopic groups. Successful incorporation of MPTI into a
6 SIPN via *in situ* polymerization during the membrane fabrication process was verified by NMR
7 spectroscopy. Compared with the Nafion membrane, the composite membrane showed
8 substantially enhanced water uptake (66.61% increase at 40% RH and 90.04% increase at 95%
9 RH) owing to the superior hygroscopicity of MPTI. Thus, the water environment in the composite
10 membrane is optimized to facilitate the dissociation of protons and the formation of hydrogen bond
11 networks for high-speed proton conduction. Furthermore, excessive area swelling was suppressed
12 by the cross-linking interactions introduced by the SPIN, and the mechanical strength of the
13 membranes in water was also preserved. As a result, the proton conductivity of the composite
14 membrane increased by up to two orders of magnitude at low humidity (189.1 mS cm^{-1} at 100%
15 RH and $0.0488 \text{ mS cm}^{-1}$ at 10% RH for Nafion; $229.67 \text{ mS cm}^{-1}$ at 100% RH and 1.66 mS cm^{-1} at
16 10% RH for Nafion/MPTI-9). Remarkably, the single fuel cell performance at 60% RH was
17 increased by 41.9% when Nafion/MPTI-9 was employed as the PEM. These findings provide a
18 practical approach for advancing fuel cell performance at low humidity.

20 ASSOCIATED CONTENT

21 **Supporting Information.** Morphologies of membrane cross sections, mechanical properties of
22 membranes, microphase separation in membranes, and thermal stabilities of membranes.

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Notes

The authors declare no competing financial interest.

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