Proton Conductivity of Proton Exchange Membrane Synergistically Promoted by Different Functionalized Metal–Organic Frameworks

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Supporting Information

ABSTRACT: In this study, two functionalized metal–organic frameworks (MOFs), UiO-66-SO3H and UiO-66-NH2, were synthesized. Then, different composite proton exchange membranes (PEMs) were prepared by single doping and codoping of these two MOFs, respectively. It was found that codoping of these two MOFs with suitable sizes was more conducive to the proton conductivity enhancement of the composite PEM. A synergistic effect between these two MOFs led to the formation of more consecutive hydration channels in the composite PEM. It further greatly promoted the proton conductivity of the composite PEM. The proton conductivity of the codoped PEM reached up to 0.256 S/cm under 90 °C, 95% RH, which was ∼1.17 times higher than that of the recast Naion (0.118 S/cm). Besides, the methanol permeability of the codoped PEM was prominently decreased owing to the methanol trapping effect of the pores of these two MOFs. Meanwhile, the high water and thermal stabilities of these two MOFs were beneficial to the high proton conductivity stability of the codoped PEM under high humidity and high temperature. The proton conductivity of the codoped PEM was almost unchanged throughout 3000 min of testing under 90 °C, 95% RH. This work provides a valuable reference for designing different functionalized MOFs to synergistically promote the proton conductivities of PEMs.

KEYWORDS: metal–organic frameworks, codoping, synergistic effect, proton conductivity, proton exchange membrane

1. INTRODUCTION

Due to the vital role in biological systems and the potential applications in proton exchange membrane fuel cells (PEMFCs), proton conduction has received great attention. The preparation of solid proton conductors is a fascinating research field especially for the application in PEMFCs. In terms of this purpose, large numbers of studies have been focused on introducing proton conductors into membrane matrices for enhancing the proton conductivities of PEMs.

Metal–organic frameworks (MOFs) have been one of the most attractive porous materials since their inception. They have shown their striking potential in catalysis, sensors, separation, gas storage, and other fields. Their arresting characteristics include adjustable pore sizes, regular void cages, and tunable surface properties. In such systems, proton conducting sites (proton donors and acceptors) can be arranged within the framework. This is favorable to the evolution of solid proton conductors for PEMs. Therefore, the potential applications of MOFs in proton conduction draw much attention. Two methods are generally used to promote the proton conduction of MOFs. The first method is encapsulation of guest molecules, such as imidazole, triazole, hydronium ions, or histamine, in the pores of MOFs. The encapsulated guest molecules and the lattice water molecules in MOFs can form a hydrogen bonding network for proton transfer. The second approach is modification of organic ligands with special functional groups. The functional groups can work as effective proton conducting sites. The latter method can make the proton conducting sites be held more securely owing to covalent linkages between functional groups and ligands.

However, the proton conduction of MOFs is restricted by their bulk phase and particle boundaries, and these two factors make proton conducting pathways of MOFs not consecutive. To better realize the proton conduction value of MOFs, functional group decorated MOFs were incorporated into polymers that can afford enough proton conducting domains to obtain proton exchange membranes (PEMs) with high proton conductivities. For instance, Xu’s group prepared a mixed-matrix Fe-MIL-101-NH2-sulfonated poly(2, 6-dimethyl-1,4-phenylene oxide) (SPPO) membrane. The proton conductivity of the resultant mixed-matrix membrane (0.10 S cm⁻¹) was increased by 25% at ambient temperature, compared to that of the SPPO membrane (0.08 S cm⁻¹). Zhu’s group assembled polypyrrole MOF with a phosphonate–functionalized MOF to obtain MOF–polymer composite PEM. The proton conductivity of the composite membrane was 2.8 × 10⁻⁵ S cm⁻¹ at 298 K and ∼53% RH, which was greatly higher.
than that of pure PVP membrane (1.4 × 10⁻⁸ S cm⁻¹) under similar conditions. Jiang’s group embedded sulfonated MIL-101(Cr) into sulfonated poly(ether ether ketone) (SPEEK) to prepare hybrid PEM. The proton conductivity of the hybrid PEM was as high as 0.306 S cm⁻¹ at 75 °C and 100% RH, which was ∼2 times as much as that of SPEEK membrane (0.156 S cm⁻¹).⁵²

Among the reported MOF hybrid PEMs, amino-functionalized MOFs and sulfonate-functionalized MOFs have been verified to be two kinds of excellent candidates for effectively enhancing the proton conductivity of PEM. The sulfonic acid groups of MOFs can endow the PEM with more proton conducting sites.²²,²³ They can also bond with water molecules at the interfaces of polymer/MOFs to provide extra proton transfer pathways.²⁴,²⁵ The amino groups of MOFs can function as effective proton transfer sites, which are favorable to proton conduction.

Herein, different composite PEMs were fabricated by single doping and codoping of sulfonate-functionalized MOF and amino-functionalized MOF (UiO-66-SO₃H and UiO-66-NH₂). Specifically, UiO-66-SO₃H and UiO-66-NH₂ possess higher stabilities than MIL-101-SO₃H and MIL-101-NH₂ (two other good candidates for proton conduction) to some extent. Besides, the pores of MIL-101-SO₃H and MIL-101-NH₂ are slightly smaller than those of UiO-66-SO₃H and UiO-66-NH₂. Protons may pass through slightly bigger pores more easily.²⁵ So, UiO-66-SO₃H and UiO-66-NH₂ were selected to facilitate the proton conduction of PEM in this work. Among the composite PEMs, the codoped PEM exhibited the highest enhancement of proton conductivity. This was attributed to the fact that the synergistic effect between UiO-66-SO₃H and UiO-66-NH₂ led to the formation of more consecutive hydration channels in the codoped PEM. It greatly promoted the proton conductivity of the codoped PEM under high humidity. Its proton conductivity reached up to 0.256 S/cm under 90 °C, 95% RH, which was ∼1.17 times higher than that of the recast Nafion (0.118 S/cm). Additionally, the high water and thermal stabilities of UiO-66-SO₃H and UiO-66-NH₂ guaranteed an excellent proton conductivity stability of the codoped PEM. The effect of MOF sizes on the proton conductivities was also investigated. It was found that smaller MOFs were more conducive to the proton conductivities of composite PEMs. This could be ascribed to a better match of smaller MOFs with the ionic clusters. Meanwhile, the methanol trapping effect of these two MOFs made the methanol permeability of the codoped PEM reduce distinctly. To the best of our knowledge, this is the first work regarding synergistic promotion of the proton conductivity of PEM by different functionalized MOFs. This work may provide a valuable guideline for designing different functionalized MOFs to synergistically promote the proton conductivities of PEMs.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterizations. All the reagents were commercially provided and used without further purification. FTIR spectra were recorded on Nicolet Nexus 470 spectrometer. XRD patterns were collected on a Bruker D8 ADVANCE and DAVINCI DESIGN diffractometer. A thermal analyzer (PerkinElmer, N2 atmosphere) was used to obtain thermogravimetric (TG) curves. Transmission electron microscopy (FEI Tecnai G2 20 TWIN) was applied to observe the morphologies of UiO-66-NH₂ and UiO-66-SO₃H. Atomic force microscope images (Multimode 8) were received at the interfaces of polymer/MOFs to provide extra proton transfer pathways.²⁴,²⁵

2.2. Membrane Preparation. First, UiO-66-NH₂ (∼40 nm) and UiO-66-SO₃H (∼100 nm) were dispersed homogeneously in DMF, respectively. Second, rotary evaporation was used to replace the solvent of the as-received Nafion solution (50 mg/mL) with DMF. UiO-66-NH₂ (∼40 nm)/DMF and UiO-66-SO₃H (∼100 nm)/DMF solutions were added into the Nafion/DMF solutions, respectively. Then, the mixtures were treated by ultrasonication for at least 1 h to obtain the corresponding casting solutions. The subsequent procedures could be obtained from our previous work.²⁹ For convenience, the as-prepared membranes were named UiO-66-NH₂ (∼40 nm)/Nafion-x and UiO-66-SO₃H (∼100 nm)/Nafion-x, where x denoted the weight percentage of the incorporated particles based on the Nafion matrix (0.3%, 0.6%, or 0.9%). In addition, UiO-66-NH₂/Nafion-0.6 membranes containing different UiO-66-NH₂ sizes (∼90 and ∼140 nm) were also prepared via the same procedures, respectively. The corresponding membranes were named as UiO-66-NH₂ (Y nm)/Nafion-0.6, where Y represented the particle size of UiO-66-NH₂. In addition, UiO-66-SO₃H/Nafion-0.6 containing ∼200 nm of UiO-66-SO₃H was also prepared via the same procedures. The corresponding membrane was named as UiO-66-SO₃H (∼200 nm)/Nafion-0.6. Specifically, UiO-66-NH₂ and UiO-66-SO₃H, respectively, denote UiO-66-NH₂ (∼40 nm) and UiO-66-SO₃H (∼100 nm) in the following descriptions, unless otherwise stated. Additionally, the composite PEMs codoped by different molar ratios of UiO-66-NH₂ and UiO-66-SO₃H were also prepared under the same condition to explore the suitable ratio of codoping. The total doping amounts were all 0.6 wt % based on the weights of Nafion. The corresponding codoped PEMs were named as UiO-66-NH₂:UiO-66-SO₃H (1:1)/Nafion-0.6, UiO-66-NH₂:UiO-66-SO₃H (2:1)/Nafion-0.6, and UiO-66-NH₂:UiO-66-SO₃H (3:1)/Nafion-0.6, respectively. For simplicity,
crystalline (2θ = 17° ± 0.6, and UiO-66-NH2 + UiO-66-SO3H/Naion-0.6).

**3. RESULTS AND DISCUSSION**

**3.1. Preparation and Characterization of UiO-66-NH2 and UiO-66-SO3H.** Solvothermal reaction was used to prepare UiO-66-NH2 and UiO-66-SO3H. The detailed preparation procedures are described in SI. In addition, the reasons why smaller UiO-66-NH2 and UiO-66-SO3H can be obtained under higher reactant concentration are also given out in SI. The morphologies of UiO-66-NH2 and UiO-66-SO3H are shown in Figure 1a,b, respectively. The sizes of these two MOFs are ~40 and ~100 nm, respectively. Figure 1c presents the XRD patterns of UiO-66 (simulated), UiO-66-NH2, and UiO-66-SO3H. They are extremely similar, which indicates the successful preparation of UiO-66-NH2 and UiO-66-SO3H.

Furthermore, UiO-66-SO3H with the size of ~200 nm (Figure 2a) and UiO-66-NH2 with the sizes of ~90 and ~140 nm (Figure 2b,c) were, respectively, prepared to investigate the effect of MOF size on the proton conduction of composite PEMs.

**3.2. Characterization of PEMs (XRD Patterns, TGA Results, Cross-Sectional FE-SEM Images, and SWs).** The microstructural transformations of PEMs can be effectively characterized by XRD. A characteristic broad peak at 2θ = ~17° appears in the XRD pattern of the recast Naion (Figure 3). It is an integration of amorphous (2θ = ~16.1°) and crystalline (2θ = ~17.7°) domains of Naion. For the XRD patterns of UiO-66-SO3H/Naion-0.6, UiO-66-NH2/Naion-0.6, and UiO-66-NH2 + UiO-66-SO3H/Naion-0.6, this characteristic peak moves to slightly smaller 2θ locations. This can be ascribed to the impeded crystallization of Naion backbones by the strong interactions between UiO-66-SO3H (or/and UiO-66-NH2) and Naion.

The TGA results (Figure 4a,b) disclose that the thermal stability of Naion backbones can be enhanced by the incorporation of UiO-66-SO3H or/and UiO-66-NH2. This may be rooted in the strong interactions between the incorporated particles and Naion. Additionally, the restraint effect of the added particles on the diffusion of decomposed products may be also conducive to the enhancement of thermal stability to some extent.

Diblock morphology that resulted from the bicontinuous microstructure appears in the cross-sectional FE-SEM image of the recast Naion (Figure S3a). This characteristic morphology becomes more obvious in UiO-66-SO3H/Naion-0.6 (Figure S3b), UiO-66-NH2/Naion-0.6 (Figure S3c), and UiO-66-NH2 + UiO-66-SO3H/Naion-0.6 (Figure S3d). This may be attributed to the strong interactions between Naion and the added MOFs, which have been verified by XRD and TGA. The strong interactions make the nonuniformity of Naion microstructure more obvious.

The SWs of the aforementioned three composite PEMs are illustrated in Figure 5. Both the SWs in water and methanol of the three composite PEMs decrease, compared to those of the recast Naion. It indicates that UiO-66-NH2 and UiO-66-SO3H can restrain the motion of polymer chains, which is beneficial to the structure stability of PEMs.

**3.3. Proton Conductivities of PEMs.** Figure 6a,b presents the temperature-dependent proton conductivity of the recast Naion at 95% RH. Clearly, the proton conductivity of the recast Naion is enhanced slowly with increasing temperature. The proton conductivities of all the composite membranes in Figure 6 increase faster than that of the recast Naion with the temperature increasing at 95% RH. Additionally, all the composite membranes show greater proton conductivities under the same conditions, compared to that of the recast Naion. From Figure 6a,b, the appropriate incorporation amounts of both UiO-66-SO3H and UiO-66-NH2 are 0.6 wt %, because UiO-66-SO3H/Naion-0.6 and UiO-66-NH2/Naion-0.6 exhibit the highest proton conductivities under the same conditions among UiO-66-SO3H doped PEMs and UiO-66-NH2 doped PEMs, respectively. Specifically, the proton conductivities of UiO-66-SO3H/Naion-0.6 and UiO-66-NH2/Naion-0.6 are higher than that of UiO-66/Naion-0.6 reported in our previous work. This is ascribed to the improved water retention capacity by amino groups and sulfonic acid groups. It further increases the proton conductivities of UiO-66-SO3H/Naion-0.6 and UiO-66-NH2/Naion-0.6 under high humidity.

Obviously, smaller UiO-66-SO3H and UiO-66-NH2 are more beneficial to the proton conductivity enhancement of...
composite PEMs (Figure 6a,c). A better match of smaller MOFs with the ionic clusters of PEMs may be responsible for it.\textsuperscript{28} Interestingly, the codoping of UiO-66-SO\textsubscript{3}H and UiO-66-NH\textsubscript{2} is more advantageous to the proton conduction, compared to their corresponding single doping (Figure 6d). The proton conductivity of UiO-66-NH\textsubscript{2} + UiO-66-SO\textsubscript{3}H/Na\textsubscript{film}-0.6 reaches up to 0.256 S/cm under 90 °C, 95% RH, which is \sim 1.17 times higher than that of the recast Na\textsubscript{film} (0.118 S/cm), and higher than those of most of MOF doped PEMs (Table S2). Specifically, the Nyquist plots of the recast Na\textsubscript{film}, UiO-66-NH\textsubscript{2}/Na\textsubscript{film}-0.6, UiO-66-SO\textsubscript{3}H/Na\textsubscript{film}-0.6, and UiO-66-NH\textsubscript{2} + UiO-66-SO\textsubscript{3}H/Na\textsubscript{film}-0.6 under 95% RH and 90 °C are displayed in Figure S4a−d, respectively.

3.4. Mechanism of Proton Conductivity Enhancement. According to the comparison result of proton conductivities in Figure 6d, we speculate that a synergistic effect exists between UiO-66-SO\textsubscript{3}H and UiO-66-NH\textsubscript{2}. The effect may make the hydrophilic areas of Na\textsubscript{film} become more consecutive. Thus, more consecutive hydration channels form in the codoped PEM. Protons pass through the continuous hydration channels more easily. It further distinctly promotes the proton conductivity of the codoped PEM. To verify the aforementioned speculation, the WUs of UiO-66-SO\textsubscript{3}H/Na\textsubscript{film}-0.6, UiO-66-NH\textsubscript{2}/Na\textsubscript{film}-0.6, and UiO-66-NH\textsubscript{2} + UiO-66-SO\textsubscript{3}H/Na\textsubscript{film}-0.6.
UiO-66-SO₃H/Nafion-0.6 were measured (Figure 7). As expected, UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 presents the highest WU. UiO-66-NH₂ and UiO-66-SO₃H are two MOFs with good water affinity, and they possess excellent water retention capacity. So, the incorporation of the two MOFs can enhance the WUs of composite PEMs, and further elevate the proton conductivities of composite PEMs under high humidity. More continuous hydration pathways in UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 resulted from the synergistic effect between UiO-66-SO₃H and UiO-66-NH₂ and better promote the WU of the composite PEM.

To more intuitively reflect the formation of more consecutive hydration channels in the codoped PEM, AFM was used to characterize the change of proton conducting areas in PEMs. This takes into consideration that hydration channels of PEMs characterize the change of proton conducting areas in PEMs. This takes into consideration that hydration channels of PEMs.

Figure 7. WUs of the recast Nafion, UiO-66-NH₂/Nafion-0.6, UiO-66-SO₃H/Nafion-0.6, and UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6.

Figure 8. LogDMTModulus AFM images of (a) the recast Nafion, (b) UiO-66-NH₂/Nafion-0.6, (c) UiO-66-SO₃H/Nafion-0.6, and (d) UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6.

Nafion, UiO-66-NH₂/Nafion-0.6, UiO-66-SO₃H/Nafion-0.6, and UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6. With the ionic clusters (relatively darker areas), the proton conducting areas gradually become more consecutive. This is coincident with the proton conductivity results (Figure 6d) and conforms to the above-mentioned speculation. It further demonstrates that the codoping of UiO-66-NH₂ and UiO-66-SO₃H is better for the promotion of proton conductivity.

3.5. Appropriate Codoping Ratio and Proton Conductivity Stability. To explore the appropriate codoping ratio of UiO-66-NH₂ and UiO-66-SO₃H, UiO-66-NH₂:UiO-66-SO₃H(1:1)/Nafion-0.6 and UiO-66-NH₂:UiO-66-SO₃H(3:1)/Nafion-0.6 were prepared under the same conditions. From Figure 9a, the molar ratio of 2:1 (UiO-66-NH₂:UiO-66-SO₃H) is more favorable to the enhancement of proton conductivity.

In consideration of the high water and thermal stabilities of UiO-66-NH₂ and UiO-66-SO₃H, which are supposed to be advantageous for the stability of excellent proton conduction in PEM under high humidity and high temperature, the proton conductivity stability of UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 was studied. As shown in Figure 9b, the proton conductivity of UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 is very stable throughout 3000 min of testing under 95% RH and 90 °C.

3.6. Methanol Permeabilities and Selectivities. Methanol permeability is another important parameter predominating the performance of PEM, because the total efficiency of the fuel cell will decrease dramatically under the permeation of methanol from anode to cathode.33,34 As presented in Table 1, the methanol permeabilities of UiO-66-SO₃H/Nafion-0.6, UiO-66-NH₂/Nafion-0.6, and UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 are all lower than that of the recast Nafion. This may be attributed to the methanol trapping effect of UiO-66-SO₃H pores and UiO-66-NH₂ pores.28,35 Especially, the selectivity (the ratio of proton conductivity to methanol permeability) of UiO-66-NH₂ + UiO-66-SO₃H/Nafion-0.6 exhibits a prominent increase under “80 v/v% methanol aqueous solution, 40 °C” harsh condition, compared to that of the recast Nafion. This further manifests the effectiveness of our obtained composite PEM codoped by UiO-66-NH₂ and UiO-66-SO₃H.

4. CONCLUSIONS

Novel PEM was prepared by codoping of UiO-66-NH₂ and UiO-66-SO₃H. The synergistic effect between UiO-66-NH₂ and UiO-66-SO₃H caused more consecutive hydration channels to be formed in the codoped PEM. It greatly promoted the proton conductivity of the codoped PEM under high humidity. The effect of UiO-66-NH₂ and UiO-66-SO₃H sizes on the proton conductivities of the composite PEMs was investigated in detail. It was found that smaller UiO-66-NH₂ and UiO-66-SO₃H were more beneficial to the proton conductivity enhancement. This may be attributed to the fact that a better match with the ionic clusters and larger specific surface area of smaller MOFs endowed PEM with higher water retention capacity. Additionally, the high water and thermal stabilities of these two MOFs guaranteed an excellent proton conductivity stability of the codoped PEM under high humidity and high temperature. Meanwhile, the methanol trapping effect of MOF pores made the methanol permeability of the codoped PEM decrease greatly. This work provides a valuable guideline for designing different functionalized MOFs to synergistically promote the proton conductivities of PEMs.
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Figure 9. (a) Temperature-dependent proton conductivities (95% RH) of composite PEMs incorporated by different ratios of UiO-66-SO3H and UiO-66-NH2. (b) Time-dependent proton conductivity (90 °C, 95% RH) of UiO-66-NH2 + UiO-66-SO3H/Naion-0.6.

Table 1. Transport Properties of the Recast Naion, UiO-66-SO3H/Naion-0.6, UiO-66-NH2/Naion-0.6, and UiO-66-NH2 + UiO-66-SO3H/Naion-0.6

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<th>PEM</th>
<th>proton conductivity (5 cm−1, 40 °C)</th>
<th>permeability (10−8 cm2 s−1, 40 °C)</th>
<th>selectivity (106 S s cm−3, 40 °C)</th>
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<td>UiO-66-SO3H/Naion-0.6</td>
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<td>UiO-66-NH2 + UiO-66-SO3H/Naion-0.6</td>
<td>0.134 ± 0.001</td>
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**REFERENCES**


