Construction of well interconnected metal-organic framework structure for effectively promoting proton conductivity of proton exchange membrane

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Abstract

To obtain proton exchange membrane (PEM) with high proton conductivities under both high humidity and anhydrous condition, interconnected UiO-66-NH₂ was tethered onto graphene oxide (GO) surfaces, and then incorporated into Nafton matrix. Thanks to tethering effect of GO surfaces and interconnection among MOF grains, well interconnected metal-organic framework (MOF) structures (GO@UiO-66-NH₂) were constructed. The structural advantage and mechanism of GO@UiO-66-NH₂ in proton conduction were explored. It was found the synergistic effect between GO and UiO-66-NH₂ with suitable particle size was especially important for promoting proton transfer. Such interconnected structure of MOF on GO also made acid/base pair pathways between –SO₃H of Nafton and –NH₂ of GO@UiO-66-NH₂ more consecutive. This was favorable to proton conduction via both vehicle mechanism and Grotthuss mechanism. The proton conductivity of the as-prepared composite membrane reached up to 0.303 S/cm under 90 °C, 95% RH, and 3.403×10⁻³ S/cm under anhydrous condition, which was about 1.57 and 1.88 times higher than that of the recast Nafton (0.118 S/cm and 1.182×10⁻³ S/cm), respectively. Furthermore, the composite membrane showed a reduced methanol permeability, which was attributed to the barrier effect of the two-dimensional GO and the trapping of methanol by UiO-66-NH₂ pores.

1. Introduction

As the sixth type fuel cell (FC), direct methanol fuel cell (DMFC) presents a great prospect by virtue of its evident superiorities, for instance high efficiency in energy conversion, moderation in operating conditions, low pollution in discharged substance and convenience in design [1–4]. Proton exchange membrane (PEM) is a pivotal component of DMFC, because it not only transfers protons but also effectively obstructs fuel crossover between the two electrodes in the FC [5]. Proton conductivity is one of the most important parameters to evaluate the performance of PEM. Enhancing the proton conductivity is a vital approach for obtaining a high-performance FC.

Generally, protons conduct through PEM via two mechanisms [6,7]: (1) Vehicle mechanism, in which protons diffuse in the form of hydration, such as H₃O⁺ and H₂O₂⁺; (2) Grotthuss mechanism (“hopping” mechanism), in which protons jump from one transfer site to the neighboring one via hydrogen bonds. Proton conduction mainly obeys the former mechanism under high humidity, where high water retention capacity can greatly enhance the proton conductivity of PEM. While proton migration mainly follows the latter mechanism under low humidity, where efficient proton hopping sites are essential to the proton conduction. To enhance the vehicle-type proton conduction in PEMs under high humidity, hygroscopic oxides such as TiO₂, SiO₂, ZrO₂, etc. are commonly incorporated into PEMs due to their improvements in water retention capacities of the PEMs [8,9]. Directly incorporating acid/base particles into base/acid polymer membrane to endow membrane with acid/base pairs for proton hopping can also promote the Grotthuss-type proton conduction in PEMs [10,11]. –SO₃H/-NH₂ acid/base pairs have exhibited their great prospects in improving proton conductivities of PEMs under low humidity [10,12].

Metal-organic frameworks (MOFs), bridged from metal and ligand units, have received wide concerns due to their notable features, e.g. tunable structure, high porosity and large surface area. They have displayed brilliant prospect in various applications including gas storage [13–16], drug deliver [17,18], separation [19,20], catalysis [21,22], and so on. Recently, the applications of MOFs in proton conduction have also attracted gradually increasing attentions. It has been demonstrated that protons can transfer through the hydrogen-bonded networks [23–25] or the functional sites loaded in the pores of MOFs [26–29]. However, their bulk phase and grain borders make the
proton conducting passageways discontinuous [30]. This restricts their practical applications to some extent. To realize greater value of MOFs in proton conduction, MOFs were doped into polymer matrices to prepare PEMs with high proton conductivity. For example, Fe-MIL-101-NH2 was incorporated into sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO). The proton conductivity of obtained composite PEM was 0.10 S cm⁻¹ at room temperature, which was 25% higher than that of SPPO membrane (0.08 S cm⁻¹) [31]. ZIF-8, poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) and poly(vinyl alcohol) (PVA) were blended to prepare ternary composite PEM. The resultant PEM exhibited proton conductivity of 0.134 S cm⁻¹ at 80 °C and fully hydrated state, which was higher than that of Nafion-117 (0.09–0.1 S cm⁻¹) [32]. Zr-MOF-808 was incorporated into Nafion to obtain modified PEM. The proton conductivity increased by 23%, compared to that of pristine Nafion membrane [33]. However, proton conducting channels between MOF grains were not consecutive by directly incorporating MOFs into membrane matrices. This is not beneficial to further promotion effect of MOFs in proton conduction. Thus, it is interesting and also a great challenge to construct continuous proton conducting channels of MOFs.

Graphene oxide (GO), a two-dimensional (2D) material, possesses abundant oxygen functional groups (e.g. epoxide, hydroxyl and carboxyl groups) and high surface area. It presents good proton conduction material. Many prior studies have demonstrated the great advantages of GO as an excellent proton conductor in the field of PEMs [1,34–38]. Recently, some PEMs modified by new GO-based proton conductors have also been developed. For example, phosphonic acid-functionalized GO (PGO) was incorporated into Nafion to improve water retention capacity and provide new proton pathways. The resultant composite PEM displayed proton conductivity of 0.277 cm⁻¹ at 100 °C and 100% RH, which was 1.2 times higher than that of unmodified Nafion PEM [39]. Sulfonated reduced GO (SRGO) was doped into sulfonated poly(ether ketone) (SPEEK) to promote proton conduction between isolated –SO₂H in SPEEK. The proton conductivity of composite membrane increased by 300% at 80 °C and 50% RH, compared to that of pristine SPEEK membrane (2.15 mS cm⁻¹) [40]. Additionally, owing to its unique structure and ductility on micro- and nanoscale, GO has been proved to be an ideal candidate for interconnecting the ionic clusters to form consecutive proton channels [41–43]. For instance, GO was modified by polydopamine (PDA) to introduce –NH₂ and –NH₂ groups and then embedded into SPEEK matrix. The high surface area and interconnected structure allowed PDA-coated GO sheets to form long-range uninterrupted pathways, ensuring efficient proton hopping [10]. Recently, another 2D material, Ti₃C₂Tx, has also been applied to form continuous proton channels in PEM. Its large aspect ratio and high surface area allowed it to interconnect ionic clusters [44]. The mechanism of interconnecting ionic clusters was similar to that of GO.

Herein, UiO-66-NH₂ (UiO: University of Oslo), linked by Zr₆O₄(OH)₄ centers and 2-aminocterephthalic ligands, was interconnected and tethered onto GO surfaces. And then GO@UiO-66-NH₂ composite was incorporated into Nafion matrix. Specifically, metal–ligand bond strength of UiO-66-NH₂ is stronger than those of MIL-53-NH₂ and MIL-101-NH₂ (two other kinds of MOFs with high stability). Thus, UiO-66-NH₂ is relatively more stable than MIL-53-NH₂ and MIL-101-NH₂ to some extent [45]. Additionally, UiO-66-NH₂ possesses octahedral and tetrahedral cages (1.1 and 0.8 nm) [46]. Its micropores are slightly larger than those of MIL-53-NH₂ (1D micropores) and MIL-101-NH₂ [47,48]. The barrier effect of proton transfer through larger 3D micropores may be relatively smaller, compared to those of smaller 3D micropores and 1D micropores. So UiO-66-NH₂ is chosen as proton conduction material in this work. The tethering effect of GO surfaces and interconnection structure among MOF particles make proton transfer channels of UiO-66-NH₂ more consecutive. This can significantly decrease the barrier effects of proton transfer under both high humidity and low humidity. Therefore, excellent water affinity and high specific surface area of UiO-66-NH₂ are beneficial to proton conduction under high humidity via vehicle mechanism. Besides, base/acid pairs can be formed between –NH₂ groups of UiO-66-NH₂ and –SO₂H groups of Nafion. It is favorable to proton conduction via Grothuss mechanism under low humidity or even anhydrous condition. The as-prepared PEM exhibits proton conductivity as high as 0.303 S/cm under 90 °C, 95% RH, and 3.403×10⁻³ S/cm under anhydrous condition, which is about 1.57 and 1.88 times higher than that of the recast Nafion (0.118 S/cm and 1.182×10⁻³ S/cm), respectively. Furthermore, the composite PEM exhibits excellent stability in proton conductivity even after 3250 min, ascribing to outstanding water stability, thermal stability, as well as high structure stability of UiO-66-NH₂. The structural advantage and mechanism of GO@UiO-66-NH₂ in proton conduction were explored. Besides, the methanol permeation of the composite membrane reduces greatly. This work provides a promising method for preparing high-performance PEM and a valuable reference for designing optimized MOF structure as proton conductor.

2. Experimental

2.1. Materials

Natural graphite powers, ZrCl₄, dopamine hydrochloride and tris(hydroxymethyl)aminomethane were purchased from Aladin (Shanghai, China). H₂O₂ solution (30 wt%), concentrated sulphuric acid and dimethylformamide (DMF) were provided by Sinopharm Chemical Reagent Co., Ltd. 2-aminoterephthalic acid was obtained by new GO-based proton conductors. Zr-MOF-808 was incorporated into Nafion to obtain modified PEM. The proton conductivity increased by 23%, compared to that of pristine Nafion membrane [33]. However, proton conducting channels between MOF grains were not consecutive by directly incorporating MOFs into membrane matrices. This is not beneficial to further promotion effect of MOFs in proton conduction. Thus, it is interesting and also a great challenge to construct continuous proton conducting channels of MOFs.

2.2. Preparation of UiO-66-NH₂

UiO-66-NH₂ with the size of ~140 nm was synthesized according to the procedures reported in a previous work [49]. First, 0.13g of 2-aminocterephthalic acid, 0.17g of ZrCl₄ and 0.8 mL of formic acid were dissolved in 8 mL of DMF. Second, the mixture was poured into a Teflon lining (25 mL) and sealed in a stainless steel autoclave. Third, the stainless steel autoclave was placed in an oven at 120 °C for 24 h, and the products were collected by centrifugation. The powder was washed by absolute CH₃OH, and then dried in a vacuum oven. The products were named as UiO-66-NH₂ (~140 nm). UiO-66-NH₂ with the sizes of ~90 nm and ~40 nm were prepared via the same procedures except that the added amounts of 2-aminocterephthalic acid were 0.26 and 0.52g, respectively. They were correspondingly denoted as UiO-66-NH₂ (~90 nm) and UiO-66-NH₂ (~40 nm), respectively. Specifically, smaller UiO-66-NH₂ was obtained under relatively higher reactant concentration. It was attributed to faster crystallization rate under higher concentration. It made the crystallization process finish faster, thus resulting in smaller size of UiO-66-NH₂.

2.3. Preparation of GO@UiO-66-NH₂

Hummers method was applied to prepare GO, and the detailed procedure had been outlined in our previous study [35]. 100 mg of GO and 50 mg of dopamine hydrochloride were dissolved in 200 mL of tris solution (pH=8.5) by sonication in ice bath for about 30 min. Then, the mixture was stirred at 25 °C for 24 h. Polydopamine (PDA) coating adhered onto the GO surfaces by self-polymerization. The self-polymerization mechanism is shown in Scheme 1. PDA-coated GO was collected by filtration and then washed repeatedly with distilled water. At last, it was dried in a vacuum freeze dryer. Specifically, GO surfaces were modified by PDA coating for facile and desired tethering of UiO-
66-NH₂ via Michael addition reaction and Schiff base reaction between UiO-66-NH₂ and PDA coating.

To obtain GO@UiO-66-NH₂, 30 mg PDA-coated GO and 90 mg UiO-66-NH₂ were dispersed in 90 mL tris solution (pH=8.5). Then, the mixture was stirred at 25 °C for 24 h. After that, the products were collected by centrifugation. At last, the products were washed thoroughly by distilled water and dehydrated by freeze drying. The preparation process of GO@UiO-66-NH₂ is shown in Scheme 2. Specifically, the resultant size of UiO-66-NH₂ onto GO surfaces could not be desirably controlled by solvothermal treatment of the precursors of UiO-66-NH₂ and GO. Additionally, satisfying distribution of UiO-66-NH₂ onto GO surfaces could not be obtained by one-pot solvothermal method.

2.4. Membrane preparation

First, GO@UiO-66-NH₂ (~40 nm) was dispersed uniformly in DMF. Second, the solvent of the as-received Nafion solution was exchanged by DMF by rotary evaporation. After adding GO@UiO-66-NH₂ (~40 nm)/DMF solution in the Nafion/DMF solution, the mixture was placed in an ultrasound bath for at least 1 h to obtain casting solution. The subsequent procedures could be obtained from our previous works [50,51]. For convenience, the as-prepared membranes were named as GO@UiO-66-NH₂/Nafion-x, where x presents the weight percentage of the incorporated particles based on Nafion matrix (0.3, 0.6 or 0.9%). Besides, GO@UiO-66-NH₂/Nafion-0.6 membranes containing different UiO-66-NH₂ sizes (~90 nm and ~140 nm) were also prepared via the same procedures, respectively. The corresponding membranes were denoted as GO@UiO-66-NH₂ (Y nm)/Nafion-0.6, where Y presents the particle size of UiO-66-NH₂. UiO-66-NH₂/Nafion-0.6, GO/Nafion-0.6 and GO+UiO-66-NH₂/Nafion-0.6 composite membranes were also prepared with the same condition. Specifically, the weight ratio of UiO-66-NH₂ to GO is about 1.6 in the GO+UiO-66-NH₂/Nafion membrane, which is in accordance with the XPS content test result of GO@UiO-66-NH₂ (~40 nm) (Table S1) and the particle sizes of UiO-66-NH₂ in UiO-66-NH₂/Nafion-0.6 and GO+UiO-66-NH₂/Nafion-0.6 are both ~40 nm. In the following sections, UiO-66-NH₂ represents the UiO-66-NH₂ with the size of ~40 nm, unless otherwise stated.

2.5. Characterizations

Nicolet Nexus 470 spectrometer was used to record FTIR spectra. Bruker D8 ADVANCE and DAVINCI.DESIGN diffractometer was applied to collect XRD patterns. Thermogravimetric (TG) experiments were carried out under N₂ atmosphere on a Perkin Elmer Thermal Analyzer. The heat treatments were performed from 50 to 700 °C at a heating rate of 20 °C min⁻¹. Field emission scanning electronic microscope (Zeiss Ultra 55) was used to view the cross-section morphologies of membranes. The morphologies of UiO-66-NH₂ and GO@UiO-66-NH₂ were observed with transmission electron microscopy (FEI Ten nan G2 20 TWIN). Scanning probe microscopic images (Multimode 8) were obtained by QN mode. Water uptakes (WUs) of membranes were calculated from the membrane weights under dry and wet conditions. Swelling ratios (SWs) of membranes were determined from the membrane areas under dry and wet conditions. The proton conductivity tests of membranes were conducted in a four-point probe device connected with electrochemical workstation CHI660D (Shanghai, China). The methanol permeability of membrane was tested in ATR-FTIR technique. The detailed experimental procedures of proton conductivity, methanol permeability, WU, and SW of membrane were detailedly described in our previous article [35].

3. Results and discussion

3.1. Characterizations of GO, PDA-coated GO, UiO-66-NH₂ and GO@UiO-66-NH₂

Fig. 1a shows the XRD patterns of GO and PDA-coated GO. The diffraction peak at about 11.2° of GO implies about 7.9 Å distance between its adjacent sheets. According to the reference, the diffraction peak of graphite centers at about 26.5°, which indicates the interlayer distance of about 3.4 Å [52]. The apparent enlargement of interlayer distance owes to the oxidation of graphite into GO. The characteristic peak of PDA-coated GO shifts to about 10.0° with the interlayer distance of about 8.8 Å, which is attributed to the modification of PDA on the GO surfaces. Fig. 1b presents the FTIR spectra of GO, PDA-coated GO and GO@UiO-66-NH₂, respectively. The appearance of four characteristic peaks at 3428 cm⁻¹ (O-H stretching vibration), 1734 cm⁻¹ (C=O stretching vibration), 1626 cm⁻¹ (O-H bending vibration) and 1406 cm⁻¹ (C-O deformation vibration) in the FTIR spectrum of GO further implies the successful oxidation of graphite into GO.
After being coated by PDA, the IR peak at 3428 cm\(^{-1}\) is wider and stronger, which is attributed to the O-H stretching vibration of catechol and N-H stretching vibration from PDA coating [55]. In addition, the peak at 1511 cm\(^{-1}\), deriving from N-H scissoring vibration of PDA, further verifies the successful coating of PDA [56]. In the FTIR spectrum of GO@UiO-66-NH\(_2\), the peak at 3428 cm\(^{-1}\) becomes much broader and stronger than that of PDA-coated GO. This can be ascribed to the introduction of -NH\(_2\) groups from UiO-66-NH\(_2\). Moreover, the triplet at 758, 654 and 570 cm\(^{-1}\), assigning from Zr-O-Zr longitudinal and transverse modes [57], emerges in the spectrum of GO@UiO-66-NH\(_2\). The FTIR spectra indicate that UiO-66-NH\(_2\) is modified on the surfaces of GO.

Fig. 2a presents the morphology of UiO-66-NH\(_2\). The size of UiO-66-NH\(_2\) is uniform and about 40 nm. In Fig. 2b, it is clear that UiO-66-NH\(_2\) has been successfully decorated onto the surfaces of GO. The high-resolution TEM image of GO@UiO-66-NH\(_2\) (Fig. 2d) apparently demonstrates that UiO-66-NH\(_2\) crystals are interconnected and loaded on the wrinkled GO layers. The XRD patterns of GO@UiO-66-NH\(_2\) (simulated), UiO-66-NH\(_2\) (as-prepared) and GO@UiO-66-NH\(_2\) are respectively shown in Fig. 2c. They are very similar, which indicates the successful synthesis of UiO-66-NH\(_2\) and GO@UiO-66-NH\(_2\). The characteristic peak of GO does not appear in the spectrum of GO@UiO-66-NH\(_2\). It may be attributed to that two stepwise reactions onto GO surfaces make GO stacks very unordered.

Fig. 3 shows the XPS wide scan spectra of GO, PDA-coated GO and GO@UiO-66-NH\(_2\), respectively. In the XPS wide scan spectrum of PDA-coated GO, N 1s peak clearly appears, compared to that of GO. This indicates the successful coating of PDA onto GO surfaces [58]. In addition, Zr 3d peak can be obviously observed in the XPS wide scan spectrum of GO@UiO-66-NH\(_2\). This indicates that UiO-66-NH\(_2\) is decorated onto the surfaces of GO [59]. To sum up, all these results verify that GO@UiO-66-NH\(_2\) is prepared successfully.

3.2. Characterization of PEMs

XRD is a powerful technique to characterize the microstructural changes of PEMs [60]. In the XRD pattern of the recast Nafion in Fig. 4a, a typical broad peak appears at \(2\theta = ~17^\circ\), which is stemmed from the combination of its crystalline domain (\(2\theta = ~17.7^\circ\)) and amorphous region (\(2\theta = ~16.1^\circ\)) [61,62]. This characteristic peak shifts slightly to lower 20 position in the XRD patterns of GO@UiO-66-NH\(_2\)/Nafion membranes. Additionally, the shift becomes more obvious with the GO@UiO-66-NH\(_2\) being incorporated. This can be attributed to the strong interactions between GO@UiO-66-NH\(_2\) and Nafion, which
impede the crystallization of Nafion backbones. Fig. 4b1 shows the transmission FTIR spectra of the recast Nafion and GO@UiO-66-NH2/Nafion membranes. With the incorporated amount of GO@UiO-66-NH2 increasing, the C=O stretching vibration corresponding to the IR peak at 1737 cm\(^{-1}\) becomes more obvious. The \(-\text{SO}_3\text{H}\) stretching vibration band at 1062 cm\(^{-1}\) can be observed in the ATR-FTIR spectrum of the recast Nafion in Fig. 4b2. It shifts to lower wavenumber with nanofillers being added, which also indicates the interactions between GO@UiO-66-NH2 (\(-\text{NH}_2\)) and Nafion (\(-\text{SO}_3\text{H}\)). The TGA results (Fig. 4c and d) reveal that the incorporation of GO@UiO-66-NH2 plays a positive effect on the thermal stability of Nafion backbones. The increase in the decomposition temperature of Nafion backbones probably results from the strong interactions between GO@UiO-66-NH2 and Nafion. Besides, the restrained diffusion of the decomposed products by GO@UiO-66-NH2 may also contribute to this positive effect to a certain extent [63].

In the cross-sectional FE-SEM image of the recast Nafion membrane, diblock morphology is usually presented due to its bicontinuous microstructure as shown in Fig. 5a1-a3 [35,50,64]. Such a characteristic morphology becomes more apparent in GO@UiO-66-NH2/Nafion-0.3 (Fig. 5b1-b3), and GO@UiO-66-NH2/Nafion-0.6 (Fig. 5c1-c3). The changes in bicontinuous microstructure of Nafion may arise from the strong electrostatic interaction between \(-\text{NH}_2\) of UiO-66-NH2 and \(-\text{SO}_3\text{H}\) of Nafion [10,12], which has been proved by XRD and FTIR. It makes Nafion microstructure nonuniform. While the microstructure becomes uniform in GO@UiO-66-NH2 at high content. Aggregation makes the interaction between \(-\text{NH}_2\) of UiO-66-NH2 and \(-\text{SO}_3\text{H}\) weak, and thus results in a decreased effect on the microstructure of membrane. Cross-sectional TEM pictures are used to characterize the dispersion of nanofillers in membranes. Fig. 5e shows that nanofillers disperse well in membrane matrix. But some obviously aggregated GO sheets appear in GO@UiO-66-NH2/Nafion-0.9 (Fig. 5f).

The temperature-dependent proton conductivity of the recast Nafion membrane at 95% RH is presented in Fig. 6a. It increases
slowly with the temperature. While the proton conductivities of all the GO@UiO-66-NH2/Nafion composite membranes elevate faster than that of the recast Nafion with the temperature. Moreover, compared to the recast Nafion, all the composite membranes exhibit higher proton conductivities at the same conditions. Particularly, the GO@UiO-66-NH2/Nafion-0.6 composite membrane shows the highest proton conductivity values. Water retaining capacity is indispensable to fast proton transfer, especially under high humidity. As shown in Fig. 6b, the distinctly promoted WUs can provide abundant water for proton migration mainly via vehicle mechanism, and hence greatly improve the proton conductivities of the composite membranes. The proton conductivity of GO@UiO-66-NH2/Nafion-0.6 is as high as 0.303 S/cm under 90 °C and 95% RH, which is about 1.57 times higher than that of the recast Nafion membrane (0.118 S/cm), and even higher than those of previous reported works regarding GO or/and MOFs modified PEMs (Table S2). However, the proton conductivity decreases when the ratio of GO@UiO-66-NH2 is 0.9 wt%. This may be caused by the aggregation of GO@UiO-66-NH2 (Fig. 5f). In addition, temperature-dependent proton conductivity comparison of UiO-66-NH2/Nafion-0.6 and UiO-66/Nafion-0.6 at 95% RH is shown in Fig. S1a. From it, UiO-66-NH2/Nafion-0.6 exhibits higher proton conductivities at the same conditions. It indicates that amino groups can improve water retention capacity and further promote proton conduction of membrane under high humidity.

![Cross-sectional FE-SEM images of recast Nafion membrane (a1-a3), GO@UiO-66-NH2/Nafion-0.3 (b1-b3), GO@UiO-66-NH2/Nafion-0.6 (c1-c3) and GO@UiO-66-NH2/Nafion-0.9 (d1-d3) composite membranes, cross-sectional TEM pictures of GO@UiO-66-NH2/Nafion-0.6 (e) and GO@UiO-66-NH2/Nafion-0.9 (f) composite membranes.](image)

![Temperature-dependent proton conductivities (95% RH), (b) WUs, and (c) swelling ratios of the recast Nafion membrane and 0.3–0.9 wt% GO@UiO-66-NH2/Nafion composite membrane.](image)
The swelling ratios of the recast Nafion and 0.3–0.9 wt% GO@Uio-66-NH2/Nafion composite membranes are shown in Fig. 6c. Swelling ratios in water and methanol of GO@Uio-66-NH2/Nafion composite membranes all decrease, compared to those of the recast Nafion membrane. It demonstrates that the motion of polymer chains can be restrained by GO@Uio-66-NH2 for structure maintenance.

To explore the structure advantages of GO@Uio-66-NH2 in proton conduction, GO/Nafion-0.6, Uio-66-NH2/Nafion-0.6 and GO+Uio-66-NH2/Nafion-0.6 composite membranes were also prepared under the same preparation parameters. Three composite membranes also exhibit improved proton conductivities (Fig. 7a). Oxygen containing groups of GO can work as proton conductors and retain water [34]. The pores of Uio-66-NH2 can store water to elevate water retaining capacity of the composite membrane. Therefore, GO and Uio-66-NH2 can both promote proton conduction via vehicle mechanism under high humidity. Additionally, GO@Uio-66-NH2/Nafion-0.6 presents the highest proton conductivity, which is greater than that of GO+Uio-66-NH2/Nafion-0.6. It implies that the promotion in proton conductivity of GO@Uio-66-NH2 is not just the contribution of GO or Uio-66-NH2 alone. Synergistic effect between particles may be more essential reason. The interconnected structure of Uio-66-NH2 onto GO as shown in Fig. 2 may promote the formation of consecutive hydration channels for proton conduction especially at high water retention capacity. Fig. 8 illustrates AFM images of the recast Nafion, Uio-66-NH2/Nafion-0.6, GO+Uio-66-NH2/Nafion-0.6, GO/Nafion-0.6 and GO@Uio-66-NH2/Nafion-0.6 composite membranes. The ionic clusters (relatively darker areas), the proton transfer channels gradually become more consecutive. This indicates that GO@Uio-66-NH2 is conducive to the construction of consecutive proton conducting channels in the PEM.

Furthermore, better matched size of Uio-66-NH2 (~40 nm) with the ionic clusters is probably another reason. To validate it, two other sizes of Uio-66-NH2 with ~90 nm and ~140 nm are synthesized (Fig. 9a and b), and then loaded on the surfaces of GO to obtain GO@Uio-66-NH2 (~90 nm and ~140 nm). As shown in Fig. 9c and d, Uio-66-NH2 (~90 nm and ~140 nm) show relatively excessive interconnection, compared to that of Uio-66-NH2 (~40 nm). It may be attributed to that the reduction of crystallization rates at low reactant concentrations makes the interconnected growth period excessive, thus resulting in excessive interconnection among the final MOF grains. Fig. 9e presents the proton conductivities of GO@Uio-66-NH2/Nafion PEMs with different particle sizes of Uio-66-NH2. It is clearly that GO@Uio-66-NH2 (~40 nm)/Nafion shows the highest proton conductivity, being greater than those of GO@Uio-66-NH2 (~90 nm and ~140 nm)/Nafion membranes. Excessive interconnection of Uio-66-NH2 (~90 nm and ~140 nm) onto GO would break the consecution of proton transfer channels and thus result in a decrease in proton conductivity. WUs of three PEMs are depicted in Fig. 9f. The PEM with smaller size of Uio-66-NH2 possesses higher water uptake. Higher specific surface area and better interconnection of Uio-66-NH2 (~40 nm) may be responsible for it. Accordingly, the synergistic effect between GO and Uio-66-NH2 with suitable particle size promotes proton transfer in GO@Uio-66-NH2/Nafion-0.6 (Fig. 11a). Therefore, the vehicle-type proton conduction of GO@Uio-66-NH2/Nafion-0.6 is promoted distinctly under high humidity.

Additionally, such interconnected structures of MOFs on GO may also make acid/base pair pathways more consecutive. The proton conductivities of the recast Nafion, GO/Nafion-0.6, Uio-66-NH2/Nafion-0.6, GO+Uio-66-NH2/Nafion-0.6 and GO@Uio-66-NH2/Nafion-0.6 composite membranes under anhydrous condition are presented in Fig. 7b. As expected, GO@Uio-66-NH2/Nafion PEM exhibits the most enhancement in proton conductivity under anhydrous condition. Interconnected acid/base pairs make the formation of consecutive proton transfer passageways and decrease the barrier effect of proton motion. Protons can jump between the proton donors (acid groups) and acceptors (base groups) via Grotthuss mechanism without water (Fig. 11b). Therefore, GO@Uio-66-NH2/Nafion-0.6 composite membrane shows greatly enhanced proton conductivity under anhydrous condition. Its proton conductivity is as high as 3.403×10⁻³ S/cm under anhydrous condition, which is about 1.88 times higher than that of the recast Nafion (1.182×10⁻³ S/cm). In addition, proton conductivity comparison of Uio-66-NH2/Nafion-0.6 and Uio-66/Nafion-0.6
under anhydrous condition is shown in Fig. S1b. It directly reflects the effect of amino groups on proton conduction under anhydrous condition. Amino groups of UiO-66-NH₂ can form base/acid pairs with sulfonic acid groups of Nafton and further improve proton conduction of membrane under anhydrous condition.

Considering the excellent water stability and thermal stability of GO@UiO-66-NH₂, which is supposed to be beneficial to high proton conductivity maintenance of PEM in high temperature and high humidity, the proton conductivity stability of GO@UiO-66-NH₂/Nafton-0.6 composite membrane was explored. As illustrated in Fig. 10, the proton conductivity of GO@UiO-66-NH₂/Nafton-0.6 composite membrane almost does not decrease after 3250 min under 90 °C and 95% RH.

Methanol permeation from the anode to the cathode can trigger a great reduction in the overall efficiency of fuel cell [65]. Therefore, a perfect PEM should possess not only high proton conductivity, but also low methanol permeability. As shown in Table 1, the methanol permeabilities of the hybrid membranes are all lower than that of the recast Nafton membrane. In particular, GO@UiO-66-NH₂/Nafton-0.6 composite membrane exhibits the lowest methanol permeability. The barrier effect of two-dimensional GO in GO@UiO-66-NH₂ can increase the tortuosity of transport passageways [63]. Meanwhile, UiO-66-NH₂ in GO@UiO-66-NH₂ could trap methanol inside its pores, thus inhibiting the permeation of methanol [66,67]. Two positive effects greatly decrease the methanol permeability of GO@UiO-66-NH₂/Nafton composite membrane. However, the methanol permeability of GO@UiO-66-NH₂/Nafton-0.9 is higher than that of GO@UiO-66-NH₂/Nafton-0.6. It can be attributed to the aggregation of GO@UiO-66-NH₂.

Fig. 9. TEM images of (a) UiO-66-NH₂ (~90 nm), (b) UiO-66-NH₂ (~140 nm), (c) GO@UiO-66-NH₂ (~90 nm), and (d) GO@UiO-66-NH₂ (~140 nm). (e) temperature-dependent proton conductivities of GO@UiO-66-NH₂ (~40, ~90, ~140 nm)/Nafton, and (f) water uptakes of GO@UiO-66-NH₂ (~40, ~90, ~140 nm)/Nafton. (The weight percentages of GO@UiO-66-NH₂ based on Nafton are all 0.6 wt%).

Fig. 10. Time-dependent proton conductivity (90 °C, 95% RH) of GO@UiO-66-NH₂/Nafton-0.6 composite membrane.
Under the “40 °C, 80 v/v% methanol aqueous solution” harsh condition, the selectivity (the ratio of proton conductivity to methanol permeability) of GO@UiO-66-NH2/Nafion-0.6 composite membrane shows a great increase, compared to that of the recast Nafion membrane [50]. This result further demonstrates that our approach is a very efficient way to prepare high-performance PEM.

4. Conclusions

High-performance PEM was prepared by incorporation of GO@UiO-66-NH2 into Nafion matrix. Consecutive proton transfer channels of UiO-66-NH2 were constructed, owing to the tethering effect of GO surfaces and the good interconnection among MOF grains. It greatly decreased the conducting barriers both of vehicle-type and Grotthuss-type proton transfer under high humidity and anhydrous condition, respectively. The high water retention capacity of UiO-66-NH2 pores greatly enhanced the proton conductivity of PEM via vehicle mechanism under high humidity. The formed acid/base pairs between –SO3H of Nafion and –NH2 of UiO-66-NH2 provided effective sites for proton hopping via Grotthuss mechanism under low humidity. The effect of UiO-66-NH2 particle size on the proton conductivities of the composite PEMs was investigated in detail. The PEM with smaller size of UiO-66-NH2 exhibited higher proton conductivity. Higher specific surface area and better match of smaller size UiO-66-NH2 may result in higher water retention capacity of PEM, which is beneficial to the proton conductivity enhancement. Moreover, the excellent water stability and thermal stability of GO@UiO-66-NH2 endowed GO@UiO-66-NH2/Nafion composite membrane with an outstanding proton conductivity stability at high temperature and high humidity. At the same time, the increased transfer channel tortuosity endowed by the barrier effect of 2D GO, and the methanol trapping of UiO-66-NH2 significantly reduced the methanol permeability of the composite PEM. This work provides a promising and facile approach to prepare high-performance PEM and a reference to design optimized MOF structure for proton conduction.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2017.03.031.

References


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