



# 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-NH<sub>2</sub> was tethered onto graphene oxide (GO) surfaces, and then incorporated into Nafion matrix. Thanks to tethering effect of GO surfaces and interconnection among MOF grains, well interconnected metal-organic framework (MOF) structures (GO@UiO-66-NH<sub>2</sub>) were constructed. The structural advantage and mechanism of GO@UiO-66-NH<sub>2</sub> in proton conduction were explored. It was found the synergistic effect between GO and UiO-66-NH<sub>2</sub> 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 -SO<sub>3</sub>H of Nafion and -NH<sub>2</sub> of GO@UiO-66-NH<sub>2</sub> 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<sup>-3</sup> S/cm under anhydrous condition, which was about 1.57 and 1.88 times higher than that of the recast Nafion (0.118 S/cm and 1.182×10<sup>-3</sup> 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-NH<sub>2</sub> 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 H<sub>3</sub>O<sup>+</sup> and H<sub>5</sub>O<sub>2</sub><sup>+</sup>; (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 TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, 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 elevate the Grotthuss-type proton conduction in PEMs [10,11]. -SO<sub>3</sub>H/-NH<sub>2</sub> 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

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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 matrixes to prepare PEMs with high proton conductivities. For example, Fe-MIL-101-NH<sub>2</sub> 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<sup>-1</sup> at room temperature, which was 25% higher than that of SPPO membrane (0.08 S cm<sup>-1</sup>) [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<sup>-1</sup> at 80 °C and fully hydrated state, which was higher than that of Nafion-117 (0.09–0.1 S cm<sup>-1</sup>) [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 matrixes. This is not beneficial to farther 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 and excellent barrier effect, making GO an attractive proton conducting 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 S cm<sup>-1</sup> at 100 °C and 100% RH, which was 1.2 times higher than that of unfilled Nafion PEM [39]. Sulfonated reduced GO (SRGO) was doped into sulfonated poly(ether ether ketone) (SPEEK) to promote proton conduction between isolated –SO<sub>3</sub>H 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<sup>-1</sup>) [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 –NH– and –NH<sub>2</sub> 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, Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, 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-NH<sub>2</sub> (UiO: University of Oslo), linked by Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> centers and 2-aminoterephthalate ligands, was interconnected and tethered onto GO surfaces. And then GO@UiO-66-NH<sub>2</sub> composite was incorporated into Nafion matrix. Specifically, metal–ligand bond strength of UiO-66-NH<sub>2</sub> is stronger than those of MIL-53-NH<sub>2</sub> and MIL-101-NH<sub>2</sub> (two other kinds of MOFs with high stability). Thus, UiO-66-NH<sub>2</sub> is relatively more stable than MIL-53-NH<sub>2</sub> and MIL-101-NH<sub>2</sub> to some extent [45]. Additionally, UiO-66-NH<sub>2</sub> possesses octahedral and tetrahedral cages (1.1 and 0.8 nm) [46]. Its micropores are slightly larger than those of MIL-53-NH<sub>2</sub> (1D micropores) and MIL-101-NH<sub>2</sub> [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-NH<sub>2</sub> 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-NH<sub>2</sub> 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-NH<sub>2</sub> are beneficial to proton conduction under high humidity via vehicle mechanism. Besides, base/acid pairs can be formed between –NH<sub>2</sub> groups of UiO-66-NH<sub>2</sub> and –SO<sub>3</sub>H groups of Nafion. It is favorable to proton conduction via Grotthuss 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<sup>-3</sup> 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<sup>-3</sup> 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-NH<sub>2</sub>. The structural advantage and mechanism of GO@UiO-66-NH<sub>2</sub> 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, ZrCl<sub>4</sub>, dopamine hydrochloride and tris(hydroxymethyl)aminomethane were purchased from Aladin (Shanghai, China). H<sub>2</sub>O<sub>2</sub> solution (30 wt%), concentrated sulphuric acid and dimethylformamide (DMF) were provided by Sinopharm Chemical Reagent Co., Ltd. 2-aminoterephthalic acid was obtained from Sigma-Aldrich. Nafion solution (perfluorinated resin solution, 5% (W/W) in lower aliphatic alcohol and water mixture, 50 mg/mL) was received from DuPont. All the reagents and solvents were commercially supplied and used as received without further purification.

### 2.2. Preparation of UiO-66-NH<sub>2</sub>

UiO-66-NH<sub>2</sub> with the size of ~140 nm was synthesized according to the procedures reported in a previous work [49]. First, 0.13g of 2-aminoterephthalic acid, 0.17g of ZrCl<sub>4</sub> 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 CH<sub>3</sub>OH, and then dried in a vacuum oven. The products were named as UiO-66-NH<sub>2</sub> (~140 nm). UiO-66-NH<sub>2</sub> with the sizes of ~90 nm and ~40 nm were prepared via the same procedures except that the added amounts of 2-aminoterephthalic acid were 0.26 and 0.52g, respectively. They were correspondingly denoted as UiO-66-NH<sub>2</sub> (~90 nm) and UiO-66-NH<sub>2</sub> (~40 nm), respectively. Specifically, smaller UiO-66-NH<sub>2</sub> 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-NH<sub>2</sub>.

### 2.3. Preparation of GO@UiO-66-NH<sub>2</sub>

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-

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