Research paper

Superprotonic conductivity of Ti-based MOFs with Brønsted acid–base pairs

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A B S T R A C T

Fuel cells technology demands high and stable proton-conductivity electrolyte materials. Here we show an effective approach of H₂SO₄ impregnation into Ti-based metal–organic framework (Ti-MOFs, (NH₂)ₓ-MIL-125 (x = 0, 1 or 2)), attains high proton-conductivity. The proton conductivity increases for increased amino functional groups on H₂SO₄@(NH₂)ₓ-MIL-125 (x = 0, 1 or 2). The superproton conductivity, attributed to the abundant dangled amino functional groups, through an enhanced Brønsted acid–base pairs with sulfonic acid. Notably, the H₂SO₄@(NH₂)ₓ-MIL-125 measured to be superprotonic conductivity of 2.2 × 10⁻⁸ S cm⁻¹ under 98% RH & 80 °C, thus competes with the most popular electrolyte, such as Nafion. In addition, the composite appeals required characteristics of easy operation, and good stability.

1. Introduction

Developing renewable/clean energy sources to replace the fossil fuels, attracts considerable attention for the increased global clean-energy demand. Thus advances the energy storage/conversion technology to figure out the energy relevant issues. Proton exchange membrane fuel cell (PEMFC) is one of the promising technology owing to the low-pollutant emission, high-energy density and mild operating conditions [1–2]. High proton-conducting electrolyte materials offer multiple advantages to make hydrogen fuel cells more efficient. At present, most of the proton conductors are based on Nafion [3], organic polymers and inorganic solid acids [4]. However, most of them are non-crystalline structures, therefore difficult to exactly analysis the structure–activity relationship, and what is more, there is a challenging to well-defined control over the high-order structures. Synthetic well-established channel and crystalline structure materials are highly desired for proton conductor [5–6].

Metal-organic frameworks (MOFs), composed of metal ions or clusters bridged together with organic ligands, are well-known for its diversity of applications involves tunable-porosity, functionality, and crystallinity [7–30]. Of which, crystallinity can be coupled with many aspects of molecular-level designs, structural optimization and transport mechanisms [6]. Meanwhile, the tunable porosity and pore-dimensions can prevent unwanted fuel crossover in a PEMFC through filling pores with water and/or proton carrier [1,31–33]. Hallmark properties of MOFs make it suitable candidate for the development of proton conductors, such as the pioneering works of H. Kitagawa [2,4,33–39], MOFs, as proton conductors, can be divided into water-assisted and water-repellent categories [2,40]. Alternatively, water-assisted proton-conducting MOFs have distinct characteristic of high performance at lower operation temperatures (20 to 80 °C) obeying the H-bond interactions with water molecules [41–42]. In general, the proton conductivity is dominated by the amount and mobility of H⁺ ions [41]. So impregnating with low volatile acids, such as H₂SO₄ or H₃PO₄ into the MOF can amplify proton donors, thereby promotes the proton conductivity through the H-bond networks [1,37,43–44]. The relatively weak interactions of acid groups and MOF framework lead to high proton migration, but these acid groups are easy to get rid of the framework during the work conditions, which results in long-term stability issues [45]. For a proton conductor, both attaining high conductivity and maintain stability at the same time is very difficult through simplified approaches. Compounds with Brønsted basic sites (such as amines) and Brønsted acid sites (such as sulfonic acid) are tentative to fall into Brønsted acid–base pairs [2,42]. Brønsted acid–base pairs play the key role achieving high and long-term proton conductivity for MOFs [4,44–45]. Thus, we succeeded in rational design of high and stable proton conductive materials by introducing acid groups into amino functional MOFs with a facile way.

In this work, chemically stable Ti-MOFs, (NH₂)ₓ-MIL-125 (x = 0, 1 or 2) were directly synthesized by a modified one-pot method [46] and
high proton-conducting complexes, $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) were successfully developed by a facile impregnation way. The unique Brønsted acid–base pairs formed between $\text{H}_2\text{SO}_4$ and amino groups of MOF linkers build high-density H-bonding networks. We propose that the abundant dangling amino functional motifs have moderate interaction with sulfonic acid groups by the formation of base pair units, which resulted high proton conductivity and stability under humidified conditions. The proton conductivity increased with the increased amino functional groups of $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2). Among them, the $\text{H}_2\text{SO}_4@(\text{NH}_2)_2$-MIL-125 exhibited the highest super-proton conductivity of $10^{-2}$ S cm$^{-1}$ at 98% RH and 80°C, competes with the most of the existed proton conductive MOFs under similar conditions.

2. Experimental details

2.1. Materials

All the chemicals and solvents used during MOF and modified MOF synthesis are commercially available and used them without further purification. Terephthalic acid (bdc), 2-Aminoterephthalate (bdc-NH$_2$) and 2, 5-diamino terephthalic acid (bdc-(NH$_2$)$_2$) were purchased from Alfa Aesar Co., China. Titanium n-butoxide (Ti(OC$_4$H$_9$)$_4$) and other solvents were procured from Shanghai Chemical Reagent Co., China.

2.2. Preparation of $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ and 2)

In order to obtain NH$_2$-MIL-125, bdc-NH$_2$ (2.172 g, 12 mmol) and titanium n-butoxide (0.208 mL, 0.6 mmol) were added in to a mixed solution containing dry DMF (18 mL) and dry MeOH (2 mL) taken in a 50 mL beaker. The above mixture was stirred at room temperature for 30 min and aliquot of 10 mL was transferred into a 20 mL teflon vessel placed in a stainless steel autoclave and heated at 150°C for 72 h. After reaction, yellow powder of NH$_2$-MIL-125 nanosheets was obtained and washed with DMF and methanol consequently, and dried at 150°C for 12 h. MIL-125 and (NH$_2$)$_2$-MIL-125 were prepared using the same protocol using the same amount of bdc ligand and bdc-NH$_2$/bdc-(NH$_2$)$_2$ ligand (molar ratio, 9:1), respectively.

The freshly made (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) samples were immersed into a 1 M of $\text{H}_2\text{SO}_4$ aqueous solution for three times with a time period of 5 min, and the obtained solid powders were collected and thoroughly washed with methanol in order to remove the residual $\text{H}_2\text{SO}_4$ and dried at 80°C. The corresponding products were labeled as $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) and used to the further characterization.

2.3. Characterisation

The morphology and structure were observed by SEM (JEOL JSM-6700F) and TEM (Tecnai F20). Powder X-ray diffraction (PXRD) was performed on a Rigaku Miniflex 600 powder diffractometer using Cu-K$\alpha$ radiation ($\lambda = 1.5418$ Å), with 1°/min and 0.02° scan width between 5 and 40° 20. UV–vis spectrum was performed on a Perkin–Elmer Lambda 950. Infrared spectrums were obtained using MOF-KBr pellets on a VERTEX70 FT-IR spectrometer. Thermogravimetric analyses were carried out at a heating ramp of 10°C/min in a N$_2$ flow (50 mL/min) using a STA449 instrument. Gas sorption isotherms were measured using a ASAP 2460 gas adsorption instrument. The highly pure N$_2$ was used in the sorption experiments, the gases isotherms was measured at 77 K. Water adsorption experiment was performed by volumetric method using a IGA100B instrument at 25°C.

2.4. Proton conductivity measurements

Typically, the $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) powders were evaluated from electrochemical impedance spectroscopy for the compressed pellets of the powdered samples at controlled humidity and temperatures. The pellets of bulk samples ($\text{H}_2\text{SO}_4@\text{MIL-125}$: 2.5 mm in diameter and 0.63 mm in thickness; $\text{H}_2\text{SO}_4@\text{NH}_2$-MIL-125: 2.5 mm in diameter and 0.72 mm in thickness; $\text{H}_2\text{SO}_4@(\text{NH}_2)_2$-MIL-125: 2.5 mm in diameter and 0.73 mm in thickness) were compressed under a pressure of ~500 Mpa to ensure good contact, then both sides of the pellet were attached to gold wires (50 μm) with silver paste. AC electrochemical impedance measurements were performed by the conventional quasi-four-probe method with a Solartron SI 1260 Impedance/Gain-Phase Analyzer. The device impedance was measured by applying 200 mV ac voltage whose frequency ($\omega$) is swept from 1 to 10$^7$ Hz in 10 steps on a logarithmic scale under controlled humidity and temperature environments. Exposure of the samples to controlled humidity and temperature environments was performed using an XK-CTS80Z (Shenzhen selenium control testing equipment corp.) humidity control oven. Experiments were performed in air, at temperatures between 40 and 80 °C while humidity levels were maintained at 98% relative humidity (RH). The impedance spectra were analyzed with ZView2 (Scribner Associates), a software which was used to generate Nyquist plots and fit the data. The proton conductivity ($\sigma$, S·cm$^{-1}$) was estimated by using the equation:

$$\sigma = \frac{L}{RS}$$

where, $L$ is the thickness, $S$ is the area of the measured plate; $R$ (Ω) is the measured resistance from the Nyquist plot. The activation energy ($E_A$) is calculated by using the conductivity data between 40 and 80 °C at 98% RH with the Arrhenius equation:

$$\ln(\sigma_T) = \ln A - \frac{E_A}{k_B T}$$

where $k_B$ and A are the Boltzmann constant and the pre-exponential factor, respectively.

3. Results and discussion

As shown in Fig. 1, (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) were directly synthesized as a crystalline powder through one-pot solvothermal method. In brief, benzenedicarboxylate-(NH$_2$)$_x$ and titanium n-butoxide were taken into a solvent mixture of dry N, N-dimethylformamide (DMF) and methanol (MeOH). The (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) immersed in 1 M $\text{H}_2\text{SO}_4$ aqueous solution and then thoroughly washed with MeOH, then dried to give the pure phase of the $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) (details see Supporting Information, SI).

The morphology and purity of (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) and $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) were confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Fig. 2 and Fig. S1), showing a homogeneous nanosheet-like morphologies. After $\text{H}_2\text{SO}_4$ treatment, the resulted $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 ($x = 0, 1$ or 2) materials became thinner and smaller when compared with the corresponding (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2).

Powder X-ray diffraction (PXRD) analysis of (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) before and after $\text{H}_2\text{SO}_4$ treatment indicates its structural stability towards acid treatment (Fig. 3a and S2). As shown in Fig. 3b and S3-4, from the instantaneous color change of MOFs after acid treatment, we found that the $\text{H}_2\text{SO}_4$ treatment process of (NH$_2$)$_x$-MIL-125 ($x = 0, 1$ or 2) was fast and irreversible with the color changed from yellow to brown for NH$_2$-MIL-125, and from dark brown to red brown for (NH$_2$)$_2$-MIL-125. It is worth noting that for the MIL-125, i.e., without amine functional groups, no significant color change was observed, clearly suggesting that the indispensable of amino groups of MOF and $\text{H}_2\text{SO}_4$ strong interactions build from Brønsted acid–base pairs formation. In the fourier transform infrared (FT-IR) spectra (Fig. 3c), a peak at 1068 cm$^{-1}$ of $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 corresponds to the symmetric vibration of $\text{SO}_4^{2-}$ and which is absent for (NH$_2$)$_2$-MIL-125 [2,4,47]. The peaks between about 2800 and 3700 cm$^{-1}$ can be ascribed to amino groups [47]. Thermo-gravimetric analysis (TGA) of the $\text{H}_2\text{SO}_4@(\text{NH}_2)_x$-MIL-125 under N$_2$ atmosphere revealed that the release
of water molecules or attached solvent when the temperature is above 100 °C, the irreversible decompose of the MOF took place at above 330–350 °C (Fig. 3d). The N2-physisorption measurements at 77 K revealed that the isotherm curves are a combination of type I and type II, which are the typical permanent microporosity. Surface area of (NH2)2-MIL-125 and H2SO4@ (NH2)2-MIL-125, obtained from the Brunauer–Emmett–Teller (BET), are 1030 ± 20 and 360 ± 20 m²/g, respectively (Fig. 3e). The decreased surface area after acid treatment for MOF reflects the reduced pore volume upon -SO3H moities insertion. H2O plays a key role, generates H-bond networks in the H2O-assisted proton conductors. So to confirm the wetability of the pores of H2SO4@ (NH2)2-MIL-125, the water vapor adsorption was performed at 25 °C (Fig. 3f), the adsorption amounts of H2O increases as the vapor pressure get increased, up to 30% mass at P/P0 = 1. The water sorption isotherms exhibited obvious hysteresis behavior, meaning that the H2O are absorbed into the micropores of H2SO4@ (NH2)2-MIL-125.

All the above results show that the good stability, strong Brønsted acid-base interaction and good wettability, enable H2SO4@ (NH2)2-MIL-125 as a potential candidate for proton-conducting materials.

3.1. Proton conductivity

The proton conductivity (σ, S cm⁻¹) of H2SO4@ (NH2)x-MIL-125 (x = 0, 1 or 2) pelletized samples were carried out by alternating-current (a.c.) impedance at controlled environment (Fig. 4a, 4c and S5). The Nyquist plots obtained were consisted of a single semicircle or arcs at high-frequency and a capacitive tail at low frequency regions. In detail, semicircle is representative of bulk and grain boundary resistance and the tails corresponding to ionic conductivity blocked by the silver electrodes [2,34,37], the conductivity was calculated from the Eq. (1).

Humidity-dependent conductivity of H2SO4@ (NH2)x-MIL-125 (x = 0, 1 or 2) were measured by maintain the sample at a constant temperature of 80 °C (Fig. 4a, 4b and S5). For H2SO4@MIL-125, H2SO4@NH2-MIL-125 and H2SO4@ (NH2)2-MIL-125, low conductivity of 1.5 × 10⁻⁸, 1.5 × 10⁻⁷, 6.7 × 10⁻⁷ S cm⁻¹ at 40% RH were obtained, respectively. The σ dramatically increased to 4.9 × 10⁻⁵, 6.4 × 10⁻⁵, 4.9 × 10⁻⁴ S cm⁻¹ at 90% RH, respectively. When the measurements conditions were set to 98% RH, the σ of H2SO4@MIL-125, H2SO4@NH2-MIL-125 and H2SO4@ (NH2)2-MIL-125 increased to 6.3 × 10⁻⁵, 4.9 × 10⁻⁴, 2.2 × 10⁻² S cm⁻¹, respectively. It’s worth

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**Fig. 1.** Schematic of the preparation of H2SO4@ (NH2)x-MIL-125 (x = 0, 1 or 2), carbon, gray; oxygen, red; nitrogen, mazarine; titanium, azure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 2.** TEM images of (a) MIL-125, (b) NH2-MIL-125, (c) (NH2)2-MIL-125, (d) H2SO4@MIL-125, (e) H2SO4@NH2-MIL-125, (f) H2SO4@ (NH2)2-MIL-125, respectively.
mentioning that the $\sigma$ of $2.2 \times 10^{-2}$ S cm$^{-1}$ of H$_2$SO$_4$@(NH$_2$)$_2$-MIL-125 can be compared with the highest $\sigma$ of MOFs/CPs proton conductor (Table 1 in SI). The proton conductivities of H$_2$SO$_4$@(NH$_2$)$_2$-MIL-125 increase with the RH, it is quasi-linearly in the low RH range of 40 ~ 80%, but rapidly increased after above 80% RH. The trend is in line with the water vapor adsorption isotherm, that is means the proton primarily migration relies heavily on the water content and through the MOFs pores [41].

The temperature-dependent proton conductivities were further examined at 98% RH. Fig. 4c and Fig. S5b and d show the Nyquist plots of the proton conductivity. The $\sigma$ for H$_2$SO$_4$@MIL-125, H$_2$SO$_4$@NH$_2$-MIL-125 and H$_2$SO$_4$@(NH$_2$)$_2$-MIL-125 were calculated to be $6.2 \times 10^{-6}$, $1.7 \times 10^{-6}$, $7.2 \times 10^{-3}$ S cm$^{-1}$, respectively, at 40 °C &98% RH. The $\sigma$ value increases with temperature and were $6.3 \times 10^{-5}$, $4.9 \times 10^{-4}$, $2.2 \times 10^{-2}$ S cm$^{-1}$ at 80 °C, respectively. The activation energy ($E_a$) is calculated by fitting the $\sigma$ data with the Arrhenius equation (Please...
check the Eq. (2). \( \text{H}_2\text{SO}_4@\text{NH}_2\text{-MIL-125} \), \( \text{H}_2\text{SO}_4@\text{NH}_2\text{-MIL-125} \) and \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) demonstrated Arrhenius behavior with an \( E_a \) of 0.44, 0.28 and 0.23 eV, respectively (Fig. 4d). \( E_a \) (0.23 eV) of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) is quite small and consistent with Nafion \( (E_a = 0.22 \text{ eV}) \), a typical hydrated proton conductors [48]. The high \( \sigma \) and low \( E_a \) at high humidity may due to the almost completely dominated of the intra-channel \( \text{H}_2\text{O} \) sites, confirming a fast ion conducting behavior between adjacent \( \text{NH}_2 \)⋯\( \text{HSO}_4 \)⋯\( \text{H}^+ \) triads, as rationalized based on the Grothhuss-type hopping mechanism [1,49–50]. But the alternative vehicular mechanism of \( \text{H}_2\text{SO}_4@\text{MIL-125} \) is associated with \( E_a \) values above 0.4 eV [41]. Temperature-dependent impedance plots of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) were reproducible during heating and cooling cycles under 98% RH, indicating good recyclability up to 4 runs (Fig. S6). PXRD analysis further confirmed that the framework of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) maintained its structural integrity after proton conductivity measurements (Fig. S7).

Another interesting result is that the \( \sigma \) gradually increased with the increasing the amino functional group of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) (x = 0, 1 or 2). The \( \sigma \) value of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) under the same conditions is much higher than those of \( \text{H}_2\text{SO}_4@\text{MIL-125} \) and \( \text{H}_2\text{SO}_4@\text{NH}_2\text{-MIL-125} \). Taking into account the change of the color of the \( \text{NH}_2\text{-MIL-125} \) (x = 1 or 2) after \( \text{H}_2\text{SO}_4 \) treatment, sulfonic acid groups (Bronsted acid sites) [1] might have formed Bronsted acid–base pairs with the existence of \( \text{NH}_2 \) group (Bronsted base sites) on the organic linkers [2]. We proposed that the included diong sulfonic acid groups will increased as amino groups increase. Finally, acid–base pair unitsplay a key role for the high proton conductivity [2].

4. Conclusions

In summary, a high proton conductive complex, \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \), was synthesized by a facile impregnation way. The unique Bronsted acid–base pairs formed between \( \text{H}_2\text{SO}_4 \) and amino group of MOF build high-density H-bonding networks. Our results demonstrated that the increased proton conductivity with the increased amino functional group of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) (x = 0, 1 or 2). The proton conductivity value of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) reaches to 2.2 × 10−5 at 80 °C & 98%RH, and can be compared to those of the best proton conductors at 80 °C & 98%RH, and can be compared to those of the best proton conductors [48]. The high conductivity of a UiO-66 framework functionalized with sulfonic acid groups by facile postsynthetic oxidation, Angew. Chem. Int. Ed. 54 (2015) 5142.

In summary, a high proton conductive complex, \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \), was synthesized by a facile impregnation way. The unique Bronsted acid–base pairs formed between \( \text{H}_2\text{SO}_4 \) and amino group of MOF build high-density H-bonding networks. Our results demonstrated that the increased proton conductivity with the increased amino functional group of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) (x = 0, 1 or 2). The proton conductivity value of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) reaches to 2.2 × 10−5 at 80 °C & 98%RH, and can be compared to those of the best proton conductors of MOFs and Nafion. The high proton conductivity of \( \text{H}_2\text{SO}_4@\text{(NH}_2)\text{2-MIL-125} \) under high humidity atmospheres can be attributed to the Bronstedacid–base pair units. The results could provide a simple yet effective way to optimize the proton conducting properties of MOFs.

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

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References


