A 3D open-framework iron hydrogenophosphate showing high proton conductance under water and aqua-ammonia vapor†

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Open-framework metal phosphates, as a popular kind of porous material, have been widely explored for their potential applications in catalysis, gas separation and magnetism.1–4 Recently, proton-conductive open-framework metal phosphates have been becoming an emerging area in the field of fuel cells, in virtue of their porous structure, good proton carriers and proton-conductive properties, as well as their unique chemical stability than MOFs. Indeed, open-framework metal phosphates have been considered to have important application prospects in fuel cells.

Herein we report the first example of the proton conductivity of an open-framework metal phosphate (NH3(CH2)3NH3)[Fe3(OH)2(HPO4)2(PO4)3].4H2O under aqua-ammonia vapor. Its optimized proton conductivity is 5 × 10−2 S cm−1 at 313 K and aqua-ammonium vapor from 1 M NH3·H2O solution. That is approximately two orders of magnitude greater than the maximum value under water vapor (8.0 × 10−4 S cm−1 at 317 K and 99% RH). The proton transfer mechanism has been proposed in terms of the structural analyses, activation energy calculations, and PXRD determinations.

High proton conductivity is one of the important properties of proton conductors. Two methods, which can promote proton conductivity of porous solid proton conductors, like MOFs, porous coordination polymers (PCPs)5–8 and covalent organic frameworks (COFs),9–11 have been well documented, including (1) through modifying the pores of the framework with functional groups (−SO3H, −COOH, etc.),12–15 (2) through introducing proton conducting chemicals or proton carriers into the pores of the MOFs and layers of these materials16–19 and (3) through varying the proton conduction environment (such as temperature, relative humidity (RH) and the vapor environment). For example, Luo20 and coauthors doped imidazole into the pores of the MOF-808, raising the proton conductivity of MOF-808 to 3.45 × 10−2 S cm−1 at 338 K and 99% RH. We introduced Na+ ions into the inter-layer of a two-dimensional layered inorganic–organic hybrid metal hydrogenophosphate (C2H10N2)[Mn2(PO4)2]·2H2O via ion exchange method. The Na+ ions sharply improve the amount of water sorption of (C2H10N2)[Mn2(PO4)2]·2H2O, and promote the formation of a dense and extensive hydrogen-bonding network with water molecules, thus the proton conductivity of the ion exchange product rises to 10−2 S cm−1 at 283 K and 99% RH.21 That was more than 900 times higher than (C2H10N2)[Mn2(PO4)2]·2H2O under the same conditions. In addition, the role of water molecule is the key to achieve high proton conductivity for water-mediated proton-conducting materials; therefore, adjusting RH is a common method to vary the proton conductivity. In general, it is found that proton conductivity increases with the rising of RH. In particular, ammonia has a molecular system most similar to that of water, specifically three proton donor sites and one acceptor site with a tetrahedral geometry, a small molecular size (kinetic diameter 2.60 Å) and a degenerate conjugate acid–base system (NH4+ + NH3 ↔ NH3 + NH4+).22,23 Therefrom, we can speculate that ammonia may be a nest promising proton conducting medium. Very recently, Li22,23 group reported the proton conductivity of two isomorphic 3D COFs under aqua-ammonia vapor, both displays that the proton conductivities under aqua-ammonia vapor...
ammonia vapor are significantly enhanced than those under water vapor. This exciting result inspires us to study the open-framework metal phosphates in similar situations to explore the methods to improve the conductivity.

Herein we synthesized a three-dimension metal phosphate (NH₃(CH₂)₃NH₃)₂[Fe₄(OH)₃(HPO₄)₂(PO₄)₃]·4H₂O (1), and investigated its proton conductivity under water and aqua-ammonia vapor. Our investigation shows that 1 exhibit high proton conductivity in water vapor; then in the aqua-ammonium vapor, proton conductivity sharply increased and reached 5 × 10⁻² S cm⁻¹ (at 313 K and under aqua-ammonium vapor from 1 M NH₃ solution).

Compound 1 crystallizes in the tetragonal space group I₄₁/a, its asymmetric unit contains two crystallographically independent Fe ions (labeled as Fe(1) and Fe(2)), one HPO₄²⁻ ion (labeled as P(1)), two different PO₄³⁻ ions (labeled as P(2) and P(3)), four coordination water molecules (labeled as O(13), O(14), O(15) and O(16)) and together with two protonated propylenediammonium.

As shown in Fig. 1a, two Fe atoms (Fe(1) and Fe(2)) are both coordinated with six oxygen atoms to form FeO₆ octahedra, respectively. Fe(1) is hexacoordinated by three oxygen atoms from PO₄³⁻ anions, one oxygen atoms from HPO₄²⁻ anions and another two bridging oxygen atoms from OH⁻. Different with that, Fe(2) is ligated by two oxygen atoms from PO₄³⁻ anions, two oxygen atoms from HPO₄²⁻ anions and the rest two bridging oxygen atoms from OH⁻. The connectivity of the three PO₄³⁻ tetrahedral are shown in Fig. 1b. For HPO₄²⁻ (P1) and PO₄³⁻ (P2), three oxygen atoms connected with three Fe²⁺, respectively, and the rest oxygen atoms naked; while for PO₄³⁻ (P3), all oxygen atoms are connected with Fe²⁺.

Two crystallographically different Fe₂O₆ edge-sharing octahedro into a dimer and it further linked with two Fe(1) O₆ octahedral into a Fe₄O₂₀ cluster unit (Fig. 1a). Along the a-axis, the Fe₄O₂₀ cluster unit form an infinite chain via −Fe(1)−O(12)−Fe(1)− bonds with the neighboring two tetromers (Fig. 1c); the chains are interlinked with each other via phosphate tetrahedral to generate a three-dimensional framework structure with large tunnels parallel to (1 0 0) and the diprotonated 1,3-diaminopropane and water molecules order arranged in the channel along the a-axis (Fig. 1d).

As indicated in Fig. 2, 1,3-diaminopropane and water molecules located at the channel via hydrogen bonding interaction. Water molecules are assembled into an infinite chain parallel to a-axis in the sequence O15W–O16W–O16W–O15W–O13W–O13W–O14W and with O⋯O distances vary from 2.448 to 2.580 Å, which are much shorter than 2.850 Å in liquid water. Then, the short O⋯N distances with dO(14)⋯N(2) = 2.558 Å exist in the 1,3-diaminopropane and water molecules, and dN(1)⋯O(1) = 2.840 Å, dN(1)⋯O(2) = 2.964 Å, dN(1)⋯O(3) = 2.918 Å, dN(1)⋯O(6) = 2.931 Å, dN(1)⋯O(8) = 3.044 Å and dN(2)⋯O(10) = 2.763 Å between 1,3-diaminopropane and the
inorganic framework. Such highly ordered infinite water chains and strong hydrogen bonding interaction between 1,3-diaminopropane and inorganic framework are the potential proton conducting pathway.

Fig. S1† shows the PXRD profiles of 1 and its sample after exposure in water solution for a month, together with the simulated PXRD pattern of 1. All of the profiles show high similarity, which indicates that 1 has ultrastong storage stability. TG and DTA curves of 1 are displayed in Fig. S2.† Three-step decomposition process appeared in the TG curves. The first decomposition step in the range of 298–400 K exhibited 8.3% weight loss, which is close to the calculated value (7.96%) that corresponds to the loss of crystal water in 1. This weight-losing process is demonstrated in the DTA plot of 1, in which a peak temperature at 380 K is associated with this process. The second decomposition process starting at 400 K can be attributed to the loss of –OH groups in the inorganic framework. The rest decomposition step that started at 503 K corresponds to the decomposition of charge-compensating cations. The TG and DTA results demonstrated that 1 is thermally stable below ca. 500 K.

The temperature dependence of PXRD profiles are shown in Fig. S3.† The PXRD patterns below 423 K are almost the same as 303 K, indicating that the structure of 1 is stable although the water molecules in 1 had lost in the temperature range of 303–400 K. As the temperature further rises to 453 K, the PXRD profiles come to slight change, the diffraction peak of (2 0 0) planes slightly shift toward to higher 2θ degree indicating that the loss of the water molecules in the framework reduces the layer distance. When the temperature reached 513 K, the framework of 1 began to collapse with the strongest diffraction peak of (1 0 1) disappeared. The PXRD datas are consistence with TG that the structure is stable before 500 K.

The ac impedance of powdered sample of 1 under different RH and temperature was carried out. Notably, as shown in Fig. S4,† the proton conductivity of compound 1 is so low (7.3 × 10⁻¹² S cm⁻¹ at 403 K and 3.1 × 10⁻¹⁰ S cm⁻¹ at 503 K) under anhydrous condition that it can be ignored. However, after the compound 1 was equilibrated at various relative humidity for 72 h, they exhibit stable conductivity values. To clarify the effect of RH on proton conductivity, the humidity-dependent Nyquist plots of the proton conductivity at 303 K and in the RH range of 60% to 99% were measured. The resultant Nyquist plots are displayed in Fig. S5.† It is to be pointed out that 1 shows unregular semi-circle in the high frequency at low humidity. Nevertheless, at high humidity, the unregular arc in the high frequency and a spike in the low frequency range were observed corresponding to the boundary resistance and a electrode contribution, respectively. Proton conductivity was calculated by fitting the Nyquist plots with the Z-View program. The calculated conductivities, shown in Fig. 3, vary from 2.1 × 10⁻⁹ S cm⁻¹ (60% RH) to 1.62 × 10⁻⁸ S cm⁻¹ (75% RH), and reach a maximum value of 4 × 10⁻⁷ S cm⁻¹ (99% RH). The results indicate that the proton conductivity of 1 is humidity-independent and the conductivity value increases with increasing RH, which may be attribute to the increasing amount of water molecules at high humidity can form more H-bonds with 1, and promote the transport of protons, increasing the conductivity.

We further measured the Nyquist curves at fixed humidity (99% RH) and varied temperature range of 287 K and 317 K (Fig. 4). The resultant resistance of 1 decreased with elevating temperature, indicating that proton conductivity increased as the rising of temperature. For example, the proton conductivity of 1 is 2.0 × 10⁻⁴ S cm⁻¹ at 287 K, while with the temperature was raised to 317 K, the proton conductivity increased to 8.0 × 10⁻⁴ S cm⁻¹, which is comparable to some recently reported MOFs, such as Zn-(m-H₄L) 1.39 × 10⁻⁴ S cm⁻¹ (at 314 K and 98% RH), PA@Tp-Azo 9.9 × 10⁻⁴ S cm⁻¹ (at 332 K and 98% RH).³⁵

Fig. 5 gives the plot of ln(σT) against 1000/T at 99% RH. The activation energies (Eₘ) for proton conduction of 1 were calculated by fitting the curve with Arrhenius equation.

\[ \ln(\sigma T) = \ln A - \frac{E_\text{a}}{k_B T} \]

In equation, the symbol σ represents the proton conductivity, Eₘ is the proton transport activation energy, kₐ is the Boltzmann constant, and A is the pre-exponential factor. The calculated Eₐ value is 0.32 eV indicating that 1 follow the Grotthuss mechanism, which may that the formation of hydrogen bonding for the immersion of water molecules into the pores.

![Fig. 3](image_url) Plots of σ vs. RH at 303 K for compound 1.
are favorable to proton hopping. Besides that, samples used for proton conductivity testing under water vapor of 1 were determined by PXRD. As shown in Fig. S1,† the PXRD peaks are similar with as-synthesized and simulated data, which demonstrates that the structure of 1 keeps robust after ac impedance determination under water vapor condition.

Based on the above descriptions, we should notice that the optimization proton conductivity of 1 \( (8.0 \times 10^{-4} \text{ S cm}^{-1} \text{ at 99% RH and 317 K}) \) is apparently smaller than the Nafion-based proton-conducting material \( (\sigma = 10^{-3} \text{ to } 10^{-2} \text{ S cm}^{-1}) \), which is the unique proton conductive material for industrial application at present, and its proton conductivity is recognized as a benchmark for transcendence. Inspired by some recent research results and the summarized methods to improve the proton conductivity of porous solids, we hope to vary the vapor environment for obtaining high proton conductivity under water vapor condition.

The conductivity of 1 under aqua-ammonia vapor, obtained from \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solutions, was performed by the ac impedance method. Fig. 6 gives the impedance spectra for 1 at 303 K and different aqua-ammonia vapors from 0.01 to 1 M of \( \text{NH}_3 \cdot \text{H}_2\text{O} \). The conductivity, calculated by fitting the Nyquist plots with ZView program, increased from \( 3.6 \times 10^{-4} \text{ S cm}^{-1} \) (0.01 M) to \( 4.5 \times 10^{-3} \text{ S cm}^{-1} \) (1 M), indicating two orders of magnitude increase with the increasing concentration of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution. Not only that, the proton conductivity of 1 also showed temperature dependent, and the resultant proton conductivity increased with elevating temperature.

For example, the proton conductivity is \( 2.2 \times 10^{-3} \text{ S cm}^{-1} \) at 283 K and it increases to \( 6.5 \times 10^{-3} \text{ S cm}^{-1} \) at 313 K with 0.1 M \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution; the proton conductivity increased from \( 2.3 \times 10^{-2} \text{ S cm}^{-1} \) (283 K) to \( 5.0 \times 10^{-2} \text{ S cm}^{-1} \) (313 K) with 1 M \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution (Fig. S6, Table S1†). These results demonstrated that both high temperature and high concentration aqua-ammonia vapor can promote the improvement of proton conductivity. The maximum proton conductivity value of 1 (5.0 \( \times 10^{-2} \text{ S cm}^{-1} \)) is comparable to that of Nafion and has exceed some reported MOFs under aqua-ammonia vapor and several MOFs containing \( \text{NH}_3 \) or \( \text{NH}_4^+ \) components, such as \( \{\text{Co}_3(-\text{DMPhIDC})_2(\text{H}_2\text{O})_n\cdot 2\text{H}_2\text{O}\} \) \( (4.11 \times 10^{-3} \text{ S cm}^{-1} \text{ at 373 K with 1.5 M NH}_3\cdot \text{H}_2\text{O solution}) \), \( \{\text{Co}_3(\text{m-BrPhIDC})_2(\text{H}_2\text{O})_n\cdot 2\text{H}_2\text{O}\} \) \( (5.07 \times 10^{-3} \text{ S cm}^{-1} \text{ at 373 K with 1.5 M NH}_3\cdot \text{H}_2\text{O solution}) \), and \( \text{Ca-PiPhtA-NH}_3 \) \( (6.6 \times 10^{-3} \text{ S cm}^{-1} \text{ at 297 K and 98% RH}) \).\(^{37}\)

It also should be noted that, even with relatively low concentration \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution (0.1 M to 0.5 M), the proton conductivity values can be promoted. For instance, the proton conductivity is \( 6.5 \times 10^{-3} \text{ S cm}^{-1} \) at 313 K with 0.1 M \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution and it is \( 1.3 \times 10^{-2} \text{ S cm}^{-1} \) at 313 K with 0.5 M \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution. That is approximately one order and two orders of magnitude greater than the proton conductivity of 1 at 317 K and 99% RH.

The activation energy of 1 under aqua-ammonia vapor was estimated by using the Arrhenius equation to fit its Nyquist plots. The \( E_a \) values are listed in Table S1† and indicating that \( E_a > 0.4 \text{ eV} \) while the \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution is less than 0.1 M \( versus E_a < 0.4 \text{ eV} \) as the \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution in the range of 0.5 M and 1 M. These results imply that the proton transfer in 1 follows an efficient Grotthuss mechanism with higher concentration of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution, while the vehicle mechanism is under lower concentration of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution. This may that higher concentration of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution form more dense hydrogen bonding network and favor to proton hopping; while lower

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**Fig. 4** Nyquist plots of compound 1 at 99% RH.

**Fig. 5** The corresponding conductivity in the form of \( \ln(\sigma T) \) vs. \( 1000/T \) for 1.

**Fig. 6** Nyquist plots of compound 1 at different concentration of \( \text{NH}_3 \cdot \text{H}_2\text{O} \) solution.
concentration of NH$_3$·H$_2$O solution form a relatively sparse hydrogen bonding network and favor to proton transport.

In addition, the PXRD patterns of samples of 1 underwent proton conductivity testing under aqua-ammonia vapor were shown in Fig. S1.† The peaks are similar with as-synthesized and simulated data of 1, demonstrating that the structure of 1 has strong stability. This is one of the important properties as a good proton conductor material in the practical application.

In summary, we successfully prepared a 3D open-framework iron hydrogenophosphate 1 with excellent thermal and chemical stability and explored its proton conduction under water and aqua-ammonia vapor. We found that compound 1 possessed high proton conductivity at room temperature, especially under aqua-ammonia vapor. The corresponding proton-conducting mechanisms under water and aqua-ammonia vapors were discussed according to experimental results. In addition, the excellent structural stability of 1 underwent electrochemical experiment under water and aqua-ammonia vapor was confirmed by PXRD measure, respectively.

Our work provides a new easy-to-execute method to drastically improve the proton conductivity of open-framework metal phosphates.

**Conflicts of interest**

There are no conflicts to declare.

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