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Short communication

An ultra-stable porous coordination polymer for water-mediated proton conduction



Man Zhu^{a,b}, Lu Han^b, Qing-Qing Wang^b, Mei-Jie Wei^b, Tan Su^{a,*}, Chun-Yi Sun^b, Xin-Long Wang^{b,*}, Zhong-Min Su^b

^a Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130021, PR China
^b National & Local United Engineering Laboratory for Power Batteries, Institute of Functional Materials Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China

GRAPHICAL ABSTRACT

A water molecules contained porous coordination polymers with excellent chemical and thermal stability was reported which shows water-mediated proton (H⁺) ion-conducting property with vehicle mechanism.



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ABSTRACT

A novel porous coordination polymer compound $[Cd_{0.5}(tpy)] \cdot 0.75H_2O$ was prepared by hydrothermal synthesis, which exhibits excellent chemical stability under various organic solvents and aqueous solution with different pH values range from 3 to 13. Benefiting from guest water molecules existing in the crystal structure, this compound shows water-mediated proton (H^+) ion-conducting with conductivity of $6.03 \times 10^{-6} \, \mathrm{S \, cm^{-1}}$ under 97% relative humidity at 95 °C. The calculated thermal activation energy (1.09 eV) and strong dependency on the humidity indicates a vehicle mechanism in the proton conduction process.

The growing consumption of natural resources, such as oil and gas, has greatly increased energy demands. The development of alternative sources of energy becomes even more urgent. Fuel cells as an alternative clean energy system are gradually gaining attention [1], out of which polymer electrolyte membrane fuel cells (PEMFCs) have been studied most [2]. The design and synthesis of new proton conducting

* Corresponding author. *E-mail addresses*: sutan_jlu@jlu.edu.cn (T. Su), wangxl824@nenu.edu.cn (X.-L. Wang).

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materials is vital to the development of PEMFCs [3]. Ideal proton conductive materials generally have the following characteristics: (i) having high proton conductivity between the electrodes to make proton exchange fleetly and efficiently, (ii) possessing excellent thermal and chemical stability to ensure the safety of internal reaction environment of battery, (iii) low cost in order to achieve industrial production and application. So far, Nafion is the most widely used proton conducting membrane with high proton conductivity $(0.1 \, \mathrm{S} \, \mathrm{cm}^{-1})$ and chemical stability under humid conditions [4–6]. However, under high temperature (higher than 80 °C), Nafion is easily dehydrated, and proton conductivity performance undergoes a sharp decrease. In addition, because of its high cost, it is not suitable for large-scale use, which affects its actual application in fuel cells.

Therefore, people are committed to exploring new materials for proton conduction. The study of porous materials, especially PCPs, have never stopped [7-11]. Proton conductivity as a new functionality of PCPs undisputedly has attracted extensive attention of late years [12–15]. And it is not difficult to speculate that plentiful PCPs materials have been reported in succession [16-24]. For instance, UiO-66(SO₃H)₂ shows super protonic conductivity of 8.4×10^{-2} S·cm⁻¹ at 80 °C [5], and the proton conductivities for the pellet of (Me₂NH₂)[Eu(L)] $(H_4L = 5-(phosphonomethyl)isophthalic acid)$ is 3.76×10^{-3} S·cm⁻¹ at 100 °C [25]. Besides contributions coming from frameworks of PCPs, guest molecules residing in the pores play important parts to the proton conductivities, as well, such as NH4+, H2SO4, H3PO4, imidazole, triazole and some other nonvolatile proton carriers [26-29]. The observed high proton conductivities are usually attributed to the enhanced hydrophilicity of pores and accelerate proton hopping. In addition, guest water molecules as proton carriers also take a special role in the watermediated proton conducting materials. Because of its amphotericity (acting as a proton donor and acceptor) and fast rotational dynamics [30-33], guest water molecules usually impart PCPs with high conductivities as long as the materials maintain hydrated and sufficient protons [34]. As proton conducting materials, stability is another significant factor affecting practical applications. However, up to now, the chemical stability of PCPs as proton conducting materials is revealed rarely.

Herein, we report a novel PCP, $[Cd_{0.5}(tpy)]\cdot 0.75H_2O(1)$ constructed on cadmium ions and 2-(1H-1,2,4-triazol-5-yl)pyrazine (tpy) ligand which shows high thermal stability, up to 400 °C, and chemical stability in both organic solvent and acidic or basic solution. The compound possesses disordered water molecules in the channels, which makes it manifest proton conductivity property under high humidity and temperature conditions. Meanwhile, the introduction of N-containing ligand is an effective way to enhance the proton conduction. As expected, compound 1 shows conductivity values of 6.03×10^{-6} S·cm⁻¹ at 95 °C and 97% RH. The observed high stability and proton conductivity of compound 1 demonstrates its potential ability for practical applications.

Compound 1 is crystallized in space group $I4_1/acd$, its asymmetric unit comprises 1/2 Cd(II) ion center, one tpy ligand and 3/4 guest water molecules. Atom Cd is hexacoordinate, featuring coordination by six N atoms which are from four tpy ligands (Fig. 1). The Cd-N distances range from 2.2696(5) Å to 2.4816(6) Å. Each tpy ligand bridges two Cd atoms in a $\mu^2 - \eta^1 : \eta^2$ fashion, resulting in a chain structure (Fig. 1c). These chains connected by $\pi - \pi$ interaction among four-edge sixmembered rings leading to the formation of a 3D network structure. The vertical distances between the two six-membered rings are 3.5263 Å and 3.5732 Å, respectively (shown in Fig. 2). The c-axis direction of the crystal structure exist one-dimensional square channels. And the pore size is about 6.90 Å \times 6.90 Å (not considering the van der Waals radii). Guest water molecules arrange in the channels with the neighboring O...O distance of 2.883 to 2.921 Å. Many kinds of hydrogen bonds are observed in the crystal structure and some of hydrogen bonds (Å) and angles (°) are shown in ESI Table S2.

The phase purities of compound 1 were established by comparison of it observed and simulated PXRD patterns. The fitting curve agrees well with the simulation one, which indicating that the obtained compound 1 is pure phase (see ESI Fig. S1). The maximum absorption peak in the UV-Vis spectra of 1 appears at 311 nm (see ESI Fig. S8).

As presented in Fig. 3a and b, the PXRD pattern of immersed samples were in good agreement with the as-synthesized sample in the pH range of 3-13, which indicating the sample remained stable within this range of pH. FT-IR (ESI Fig. S3) and UV-Vis (ESI Fig. S4) spectra also demonstrate the good stability of compound 1 under different pH.

For stability in organic solvents, fresh sample of compound **1** was soaked in different common organic solvents including methanol, ethyl acetate, acetone, acetonitrile, N,N-dmethylformamide (DMF), isopropyl alcohol and dichloromethane. As shown in PXRD patterns, the immersed sample remained structurally intact (shown in Fig. 3d). The above-mentioned results reveal that compound **1** has excellent chemical stability both in acidic and basic solution and organic condition. Moreover, the PXRD of the sample after the AC impedance test was provided (ESI Fig. S2). The unchanged PXRD pattern of compound **1**

Table 1	
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Proton conductivities at different temperatures for compound 1 under 97% RH.

T∕°C	R/Ω	$\sigma = L/RS$
35	6.396E6	7.96272E-09
45	1.051E6	4.84582E-08
55	1.982E4	2.56961E-06
75	1.063E4	4.79112E-06
95	8445	6.03074E-06



Fig. 1. (a) Representation of the Cd^{2+} coordination environments in the crystal structure of compound 1, (b) The 3D polyhedral structure of compound1with guest water molecules, (c) 1D structure connected by tpy ligands of compound 1. Red, oxygen, White, hydrogen, Blue, nitrogen, Gray, carbon, Teal, cadmium. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Download English Version:

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