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A water cluster $(H_2O)_{12}$ guested coordination polymer as proton conducting solid electrolytes

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ABSTRACT

A coordination polymer with ordered and non-acidic water-cluster guest molecules, [Zn(cis-chdc)(bpp)]·$6H_2O$ (denoted as **Zn_2-$(H_2O)_{12}$**, H_2chdc = 1,4-cyclohexanedicarboxylic acid; bpp = 1,3-bis(4-pyridyl)propane), which captures a kind of $(H_2O)_{12}$ cluster inside the cavity, is found to be an efficient proton conducting solid electrolyte. **Zn_2-$(H_2O)_{12}$** has a high conductivity of 0.241 mS·cm^{-1} at 318 K and 95% RH (relative humidity), which is higher than the other kinds of water-only guested coordination polymers (CPs). The configuration of the water clusters has been described and the role it plays in the process of proton transportation has been investigated preliminarily.

1. Introduction

On the background of urgent need for cleaner and more sustainable alternatives for traditional fossil energy, the proton exchange membrane fuel cell (PEMFC) has become a promising environment-friendly candidate. PEMFC has been applied in satellites, fuel-cell-powered vehicles, and various mobile devices, etc. As the critical factor of PEMFC's properties [1], the proton-conducting materials should be researched.

Coordination polymers (CPs) and metal-organic frameworks (MOFs) have been intensively studied [2–7] owing to their high specific surface area, high regularity, infinitive possibility of structures, etc. MOFs/CPs are expected to be a promising solid electrolyte for proton conduction [8–10] for its crystallinity, easy functionalization and convenient to extract the proton-conducting pathway and mechanism. To endow MOFs/CPs with proton conduction behavior, several methods have been applied: 1. Functionalizing the framework with acidic groups (e.g., $-SO_3H$, $-PO_3H_2$, $-COOH$) [11–14]; 2. Introduction of proton carriers, such as inorganic acid (like heteroacid [15]) and protonic molecules (e.g., imidazole, histamine) [16,17]. Most of them were operated as water-mediated proton-conducting solid electrolytes. And two theories have been agreed as mechanisms [18,19] on water-mediated proton conduction: 1. Vehicle mechanism which is the direct diffusion among particles of the protic species; 2. Grotthuss mechanism which is the hopping process of proton through the hydrogen bonds between neighboring protic molecules. According to the former study [20], influencing factors of proton conductivity for CPs could be described by the equation:

$$\sigma = zen\mu \quad (1)$$

where in the situation of proton conduction z (the valance of proton) is 1, e is the elementary charge, n is the concentration of proton, μ is the mobility of proton. So, when it comes to CPs/MOFs, the concentration of proton can be increased by regular condensed arrangement of proton generators and the proton hopping process can be promoted by traveling through the 3-D connective alleys of CPs and via long range H-bonding networks.

While in most cases for CPs, post-absorbed guests are often not well-distributed and cannot fully fill the voids in MOFs/CPs. In the meantime, the in-situ proton conductive species in CPs may not fulfill the cavities of CPs, which makes the concentration of proton still progressive. Thus, it's better to find a regular way for the arrangement of guest molecules with high concentration. Periodical channels of CPs have already made proton species travel in a light way. What's more, the regular nature of CPs along with high concentration of proton carriers could be quite beneficial for the long-range H-bond network, which makes more contribution for Grotthuss type migration of proton. According to the factors above, the arrangement of proton carriers in CP

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compounds should be considered during the selection of guests and the design of proton conductive CP compounds.

Water has been studied intensively [21] due to the fantastic and anomalous properties it exhibits. Nanoscopically, water molecules can self-assembly into various scales of water clusters which makes it adjustable to the size of each single cavity in CPs. Besides, water molecules are nucleophilic, capable of generating proton under ionization [22], very likely to form long-range H-bond networks. These properties make it quite suitable to be the guest in proton conductive CPs. Instances of various kinds of water clusters, including chair [23–25], boat [24,26], planar [27,28] forms, captured by various kinds of crystal hosts have already been reported. Among these compounds, the largest water cluster captured by a MOF is $H^+(H_2O)_{28}$ [29,30], according to reports of Zheng, etc. However, still few have studied the proton transportation property of these water clusters in crystal hosts [31–33]. On the other hand, the self-assembly of water molecules in a closely-packing way inside the CP void could increase the concentration of proton carrier, also convenient for the construction of long-range H-bond networks. Based on these factors, we studied a CP compound, **Zn_2-$(H_2O)_{12}$** [34], which has a chair-pair-like $(H_2O)_{12}$ cluster. Compared to the ionic groups and other amorphous guest molecules, $(H_2O)_{12}$ clusters are more ordered and maximize the occupancy of proton carriers. Consequently, non-acidic **Zn_2-$(H_2O)_{12}$** exhibits a comparable proton conductivity of 0.241 mS·cm^{-1} at 95% RH, 45 °C, which is comparable to that of the former reported water clusters [32] and nanoconfined water [35] (Table S1).

2. Experimental

2.1. Synthesis of Zn_2-$(H_2O)_{12}$

All chemicals commercially purchased were of reagent grade and used without further purification. **Zn_2-$(H_2O)_{12}$** was prepared by the hydrothermal method with the same procedures of our previous work [34]. $Zn(NO_3)_2{\cdot}6H_2O$, H_2chdc (H_2chdc = 1,4-cyclohexanedicarboxylic acid), bpp (bpp = 1,3-bis(4-pyridyl) propane), triethylamine (TEA) and water were mixed and sealed in a polytetrafluoroethylene(PTFE)-lined stainless-steel container, heated at 100 °C for 24 h, and then cooled to room temperature. The colorless crystals were obtained after filtration, washed with deionized water and dried at room temperature. PXRD (Fig. S1d) and FT-IR (Fig. S5) have been used to prove successful synthesis of the pure CP compound.

2.2. Physical measurements

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were carried out on a TA-Instruments Simultaneous DSC-TGA Q Series™ with a heating rate of 5 °C min^{-1} in the range of 30–600 °C under air atmosphere. Powder X-ray diffraction (PXRD) were measured at 293 K on Siemens D 5005 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation from 5° to 60°. The nitrogen gas sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II) at 77 K·The sample was activated under N_2 stream at 25 °C for 12 h. Water sorption measurements were applied on Micromeritics ASAP2020 at 25 °C. IR spectra (4000–400 cm^{-1}) were obtained in KBr discs on a Nicolet Magna 560 IR spectrometer.

2.3. Measurement and calculation for proton conductivity

Zn_2-$(H_2O)_{12}$ were fully grounded into uniform powder and then put inside a mould with an internal diameter of 10 mm and compressed into a tablet under the pressure of 20 MPa for 5 min. Then the tablet was sandwiched by two gold plate electrodes. Thickness of the tablet in this case is ~1.62 mm, measured by a vernier caliper. The alternative current (AC) impedance spectra tests were carried out on an IVIUM (Netherland) electrochemical workstation under open-circuit voltage (OCV) with a frequency range of 1 MHz to 1 Hz and a voltage amplitude of 50 mV. The relative humidity and temperature was accommodated by an HDHWHS-50 incubator. And during the variable temperature electrochemical impedance (EIS) tests, it was kept for 30 min at each temperature condition for thermal equilibrium; as for the variable humidity EIS tests, 24 h under each humidity condition for humidity equilibrium.

ZSimpView software was used to fit the impedance data to extrapolate the resistance values. Proton conductivity was calculated from the following equation:

$$\sigma = l/AR \tag{2}$$

where σ represents the ionic conductivity (S·cm^{-1}), l is the thickness and A is the cross-section area (cm^2), R is the bulk resistance (Ω) of the sample. Activation energy (Ea) was obtained by linear fitting of the equivalent transformation of the following equation:

$$\sigma T = \sigma_0 \exp\left(-\frac{Ea}{k_B T}\right) \tag{3}$$

where σ_0 is the pre-exponential factor, k_B is the Boltzmann constant, and T is the temperature.

3. Results and discussion

3.1. Structure of Zn_2-$(H_2O)_{12}$

As shown in Fig. S1a, b, c, the whole **Zn_2-$(H_2O)_{12}$** framework is orderly piled up by 1-D ladder-like chains with 3-dimensional connectivity via hydrogen bonds. On the framework of each cavity (Fig. S2), four free oxygens of the carboxyl groups points towards to the $(H_2O)_{12}$ cluster; four points to the opposite of the $(H_2O)_{12}$ cluster, which could assist the water molecules to travel through the tunnel along *c*-axis. The $(H_2O)_{12}$ is not the same as a classic clathrate-like $(H_2O)_{12}$ cluster [21], it could be divided into two hexa-rings (as shown in Fig. 1a). Different from a typical hexamer, the confined space of the cavity and the interaction with the carboxyl groups make each hexa-ring twisted from a plane into a "chair", just like the chair configuration of hexane at some extent; each two hexa-water rings crisscross each other to form a chair-pair, the $(H_2O)_{12}$. Then this chair-pair was anchored by the four inner oxygens with H-bonds among them. Thus, this structure gives a chance for all the neighboring chair-pairs along b-axis to be connected via a head-to-tail way, as shown in Fig. 1b. Moreover, the adjacent two H_2O(2 W) molecules of two neighboring $(H_2O)_{12}$ are close enough to form a H-bond, the H..O2W distance is ~2.619 Å, while the angle of O2W-H-O2W′ is ~96° [34]. Consequently, the two $(H_2O)_{12}$ is connected to some extent, when the temperature increased, Brownian movement of molecules is getting increasingly violent, the water molecules are vibrating and rotating stronger, the neighboring $(H_2O)_{12}$ clusters are more likely to bind with each other by forming a H-bond between every two adjacent H_2O(2 W). Also, the $(H_2O)_{12}$ clusters almost fulfill every single cavity (as shown in Fig. S2), that gives **Zn_2-$(H_2O)_{12}$** a high percentage of occupancy. The nitrogen sorption isotherm (Fig. S3) fit the classic classification of Type III with no hysteresis when the adsorption process proceeded to desorption, meaning the **Zn_2-$(H_2O)_{12}$** is not porous, plus its BET surface is 73 m^2·g^{-1}, meaning relatively low uptake of N_2 for this compound, which confirms that the 1D tunnel is full of water clusters, as shown in Fig. 1c.

3.2. Physical measurements

All of the major bond information in the CPs can be found in the IR spectrum. A couple of bands at 2947 cm^{-1} represent C—H of the cyclohexane rings. Peaks appearing around 1342–1408 cm^{-1} and 1508–1591 cm^{-1} belong to symmetric and asymmetric stretching vibration of (—COO$^-$) respectively. (C—N) and (C═N) group of pyridine