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

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Contents

Section 1

1. Experimental section

1.1 Chemicals and reagents

All reagents and chemicals were purchased from commercial sources and used without further purification.

1.2 Synthesis of $(NH_3(CH_2)_3NH_3)_2$ $[Fe_4(OH)_3(HPO_4)_2(PO_4)_3]\cdot 4H_2O$ (1)

The sample was hydrothermally synthesized according to the previously reported procedure. $FeCl_3\cdot 6H_2O$ (0.2027g) and H_3PO_4 (0.22mL) were dissolved in 5 mL H_2O, Propanediamine (Aldrich) was added dropwise to the above mixture to control pH≈ 6 of the solution, and then was transferred and sealed in a 25mL Parr Teflon lined stainless steel autoclave and heated at 165°C for 3 days.

1.3 Material characterizations

Power X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5418Å) in the temperature ranges of 303-493 K (30-220 °C). TGA experiments were performed using a STA449 F3 thermogravimetric analyzer in the temperature range of 298-1073 K(25-800°C) at a warming rate of 10 °C·min^{-1} under a nitrogen atmosphere and the polycrystalline samples were placed in an Al_2O_3 crucible.

1.4 Conductivity measurements

The powered sample was pressed into a pellet with a diameter of 13mm and a thickness of ca. 0.7 mm. The measurements of proton conduction at various relative humidity and different aqua-ammonia vapor were carried out using a conventional three-electrode method with a CHI 660D electrochemical workstation and the reference electrode has been shortened with auxiliary electrode, the cable connected the copper plate electrodes with the electrochemical workstation is ca. 1.2 m. The copper plate electrode is 13 mm in diameter. The frequency of the applied alternating current (ac) field ranges from 100 Hz to 2 MHz with 5 mV of signal amplitude. The DC offset is zero. The powdered pellet of sample was sandwiched between two copper plate electrodes, which is suspended in a wild-mouth bottle with a rubber stopper and water solution of salt on the bottom, such a bottle was placed in an oven.

The humidity was tuned by the concentration of salt and monitored using a humidity probe. The concentrations of aqua-ammonia vapor were obtained from various concentrations of $NH_3 \cdot H_2O$ solution. The concentrated solution of $NH_3 \cdot H_2O$ (14.80 M) was diluted bydeionized water to concentrations of 1.0, 0.5, 0.1, 0.05, 0.01M, respectively, for proton conduction determinations.

Section2

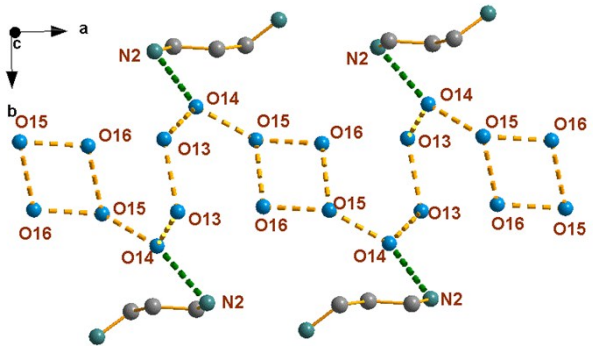

Fig. S1 Hydrogen-bonding interactions in water molecules and between water and ammonia molecules.

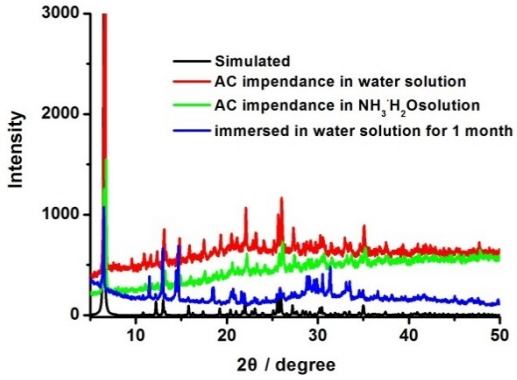

Fig. S2 X-ray diffraction profiles of **1** after ac measured

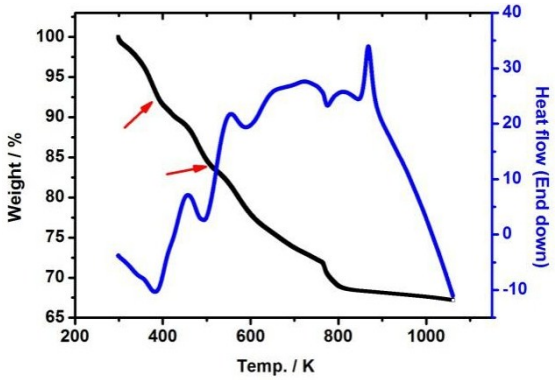

Fig. S3 TG and DTA plots of **1** in the temperature range of 298-1073 K.

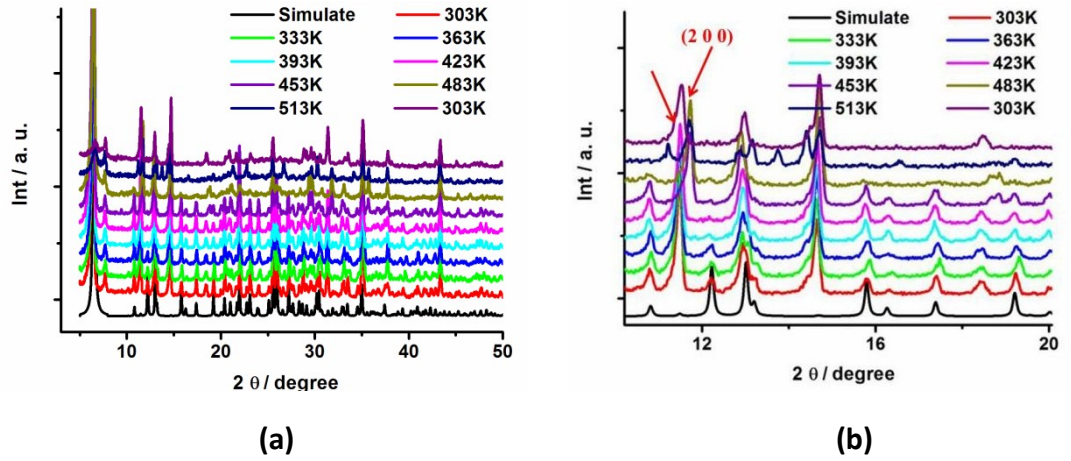

Fig. S4 Variable-temperature powder X-ray diffraction profiles of **1** with 2θ ranges of (a) 5-50° and (b) 10-20°

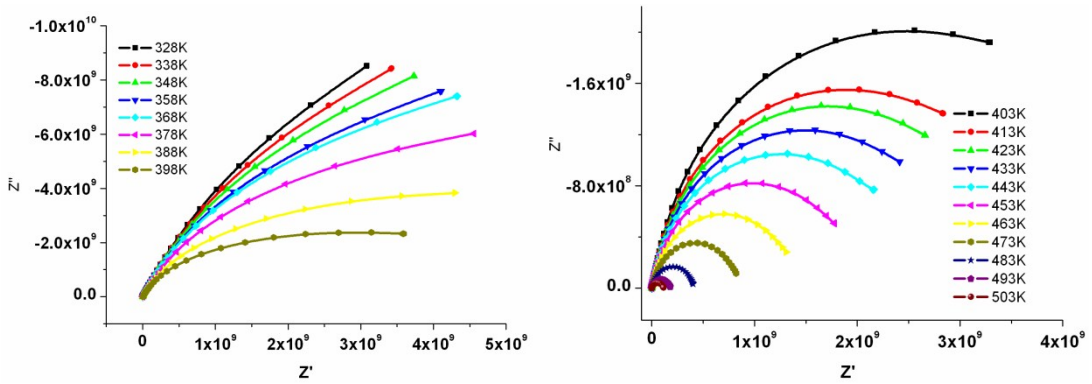

Fig. S5 Temperature dependent Nyquist plots of **1**

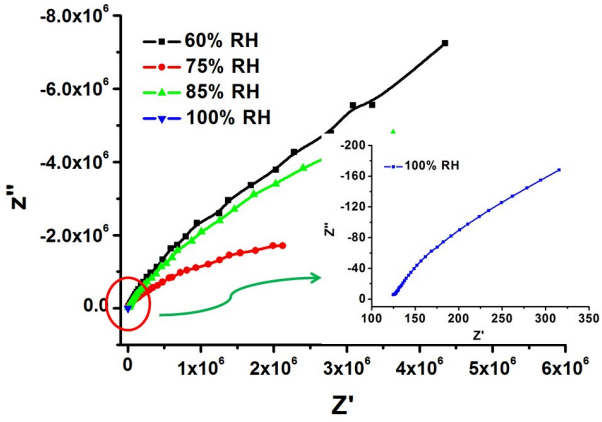

Fig. S6 Nyqusit plots of compound **1** at varied relative humidity at 303K

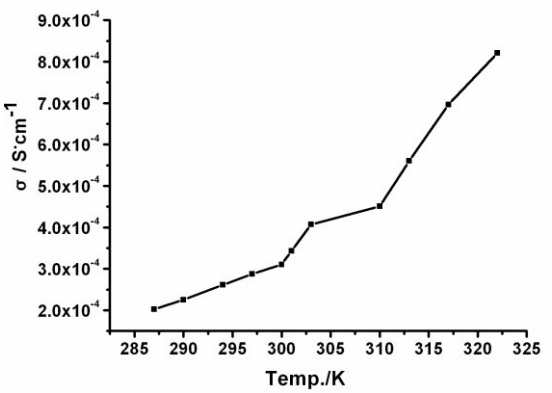

Fig. S7 The corresponding conductivity in the form of σ vs. T for **1.**

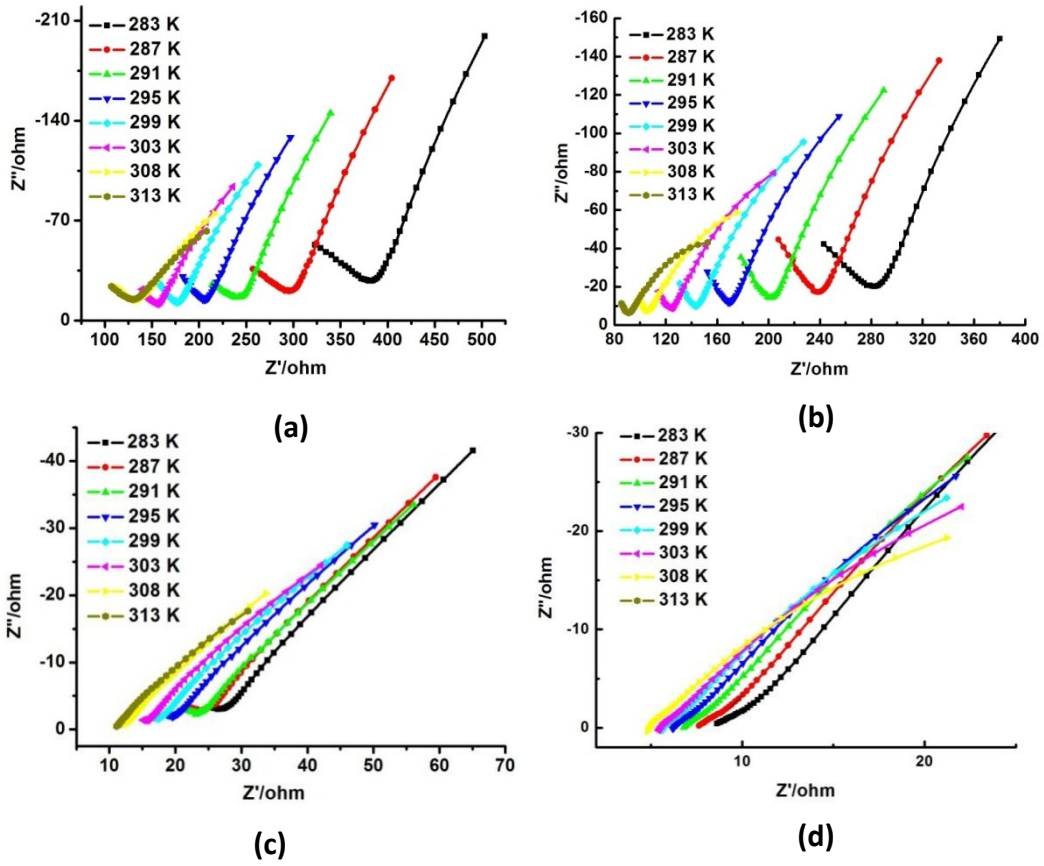

Fig. S8 Nyqusit plots of compound **1** at different centration (a) 0.01 mol·L^{-1}; (b) 0.05 mol·L^{-1}; (c) 0.1 mol·L^{-1}; (d) 0.5 mol·L^{-1} and (e) 1 mol·L^{-1} $NH_3 \cdot H_2O$ solution.

Table S1 The σ and Ea at selected $NH_3 \cdot H_2O$ solution

T/ K	0.01 mol·L^{-1}		0.05 mol·L^{-1}		0.1 mol·L^{-1}		0.5 mol·L^{-1}		1 mol·L^{-1}	
	σ / S•cm^{-1}	E_a / eV	σ / S•cm^{-1}	E_a / eV	σ / S•cm^{-1}	E_a / eV	σ / S•cm^{-1}	E_a / eV	σ / S•cm^{-1}	E_a / eV
283	1.46E-04	0.52	1.98E-04	0.51	2.26E-03	0.47	6.38E-03	0.3	2.29E-02	0.35
287	1.87E-04		2.35E-04		2.50E-03		7.14E-03		2.79E-02	
291	2.29E-04		2.77E-04		2.74E-03		7.98E-03		3.28E-02	
295	2.74E-04		3.38E-04		3.29E-03		8.81E-03		3.61E-02	
299	3.25E-04		3.96E-04		3.90E-03		9.59E-03		3.96E-02	
303	3.62E-04		4.60E-04		4.45E-03		1.00E-02		4.55E-02	
308	4.56E-04		5.38E-04		5.43E-03		1.12E-02		4.72E-02	
313	4.85E-04		6.48E-04		6.54E-03		1.27E-02		5.04E-02	