Supporting Information

Ionothermal synthesis of a highly crystalline zirconium phosphate proton conductor

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Section S1. Experimental section

All reagents were used as received from commercial suppliers without further purification. A mixture of $ZrCl_4$ (0.15 g, 0.64 mmol), H_3PO_4 (0.21 g, 2.14 mmol), $(NH_2)_2CO$ (0.15 g, 2.5 mmol), 1-Ethyl-3-methylimidazolium hexafluorophosphate ([Emim]PF_6) (0.21 g, 0.82 mmol), and 30 μL deionized water was added to a 15 mL stainless-steel PTFE autoclave liner, heated at 170 °C for 36 h in a furnace, and then cooled to room temperature. The colorless transparent rod-shaped zirconium phosphate crystal was washed with deionized water and ethanol and dried in air, with a yield of ca. 67% (based on zirconium). Elemental analyses (%) for **ZrP-3**: Calcd: C 0.000, N 8.305, H 2.668. Found: C 0.000, N 7.956, H 3.032.

Other Physical Measurements: Thermalgravimetric (TG-DSC) analysis was carried out on a NETZSCH STA 449 F3 jupiter instrument in the range of 30-900 °C under a nitrogen flow at a heating rate of 10 °C/ min. Elemental analyses (C, H, and N) were carried with a Vario EL CHNOS elemental analyzer. A Quantachrome Autosorb gas sorption analyzer (IQ2) was used to perform the water adsorption measurements.

Section S2. X-ray crystallography

Crystals of the **ZrP-3** data collection were mounted on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo Kα radiation, λ = 0.71073 Å, 50 kV/50 mA power) adopting the direct-drive rotating anode technique and a CMOS detector at 296 K. The data frames were collected using the program APEX3 and processed using the program SAINT routine in APEX3. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-2014 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms were put in calculated positions. Details of the crystal data and structural refinement can be found in Supplementary Table S1, S2 and S3.

Table S1. Crystal data and structure refinement results for **ZrP-3.**

compounds	**ZrP-3**
Empirical formula	**$(NH_4)_2[ZrF(PO_4)(HPO_4)]$**
Formula weight	672.49
Temperature (K)	296
Crystal system	Orthorhombic
Space group	P_{nma}
a (Å)	12.700(2)
b (Å)	5.1925(8)
c (Å)	14.548(2)
α	90
β	90
γ	90
V (Å^3)	959.4(2)
Z	2
F (000)	660
GOF on F^2	1.520
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0430, 0.1162
CCDC	2155003

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$.

Table S2. Bond Lengths (Å) for **ZrP-3**

Bond Length/Å			Bond Length/Å
Zr1—F1B	1.987(7)	P1—O1A	1.453(11)
Zr1—O1A	2.095(11)	P1—O1B	1.559(10)
Zr1—O1B	2.101(10)	P1—O2	1.545(8)
Zr1—O4A	2.059(10)	P1—O3B	1.484(8)
Zr1—O4B	2.016(10)	P2—O4A	1.560(10)
Zr1—O5_a	2.051(7)	P2—O4B	1.518(10)
N1—H2	0.890(3)	P2—O5	1.537(8)
N1—H2	0.880(5)	P2—O6A	1.540(6)
N1—H3	0.880(5)	P2—O6B	1.510(6)
N2—H4	0.900(5)	O1A—O1B	0.698(15)
N2—H5	0.880(7)	O4A—O4B	0.688(15)
N2—H6	0.880(9)	O6A—O6B	0.22(7)

Table S3. Distances (Å) and angles (°) of hydrogen bonding for **ZrP-3**

	Bond Length/Å		Angles/°
N1—H3···F1B	2.510(2)	2.812(9)	101(2)
N1—H3···O4A	2.330(5)	3.134(13)	152.3(19)
N2—H6···F1B	2.350(9)	2.831(12)	114(7)
N2—H6···O1B	2.470(8)	3.261(13)	149.2(18)

Section S3. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction patterns were collected from 5° to 50°, with a step of 0.02°, and the time for data collection was 0.5 s using a Bruker D8 advance X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) and a Lynxeye one-dimensional detector.

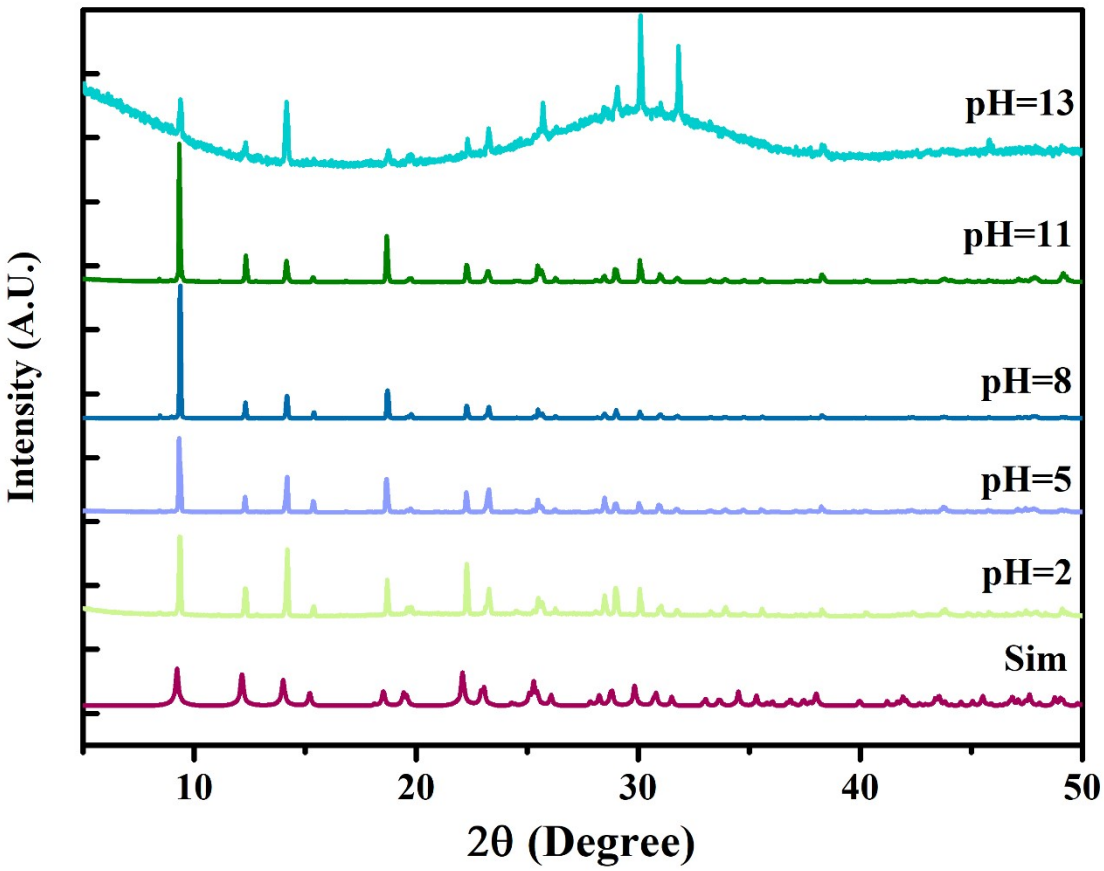

Fig. S1. PXRD patterns of the as-synthesized **ZrP-3** samples after soaked in aqueous solutions at pH ranging from 2 to 13 treatment.

Section S4. Optical microscope images

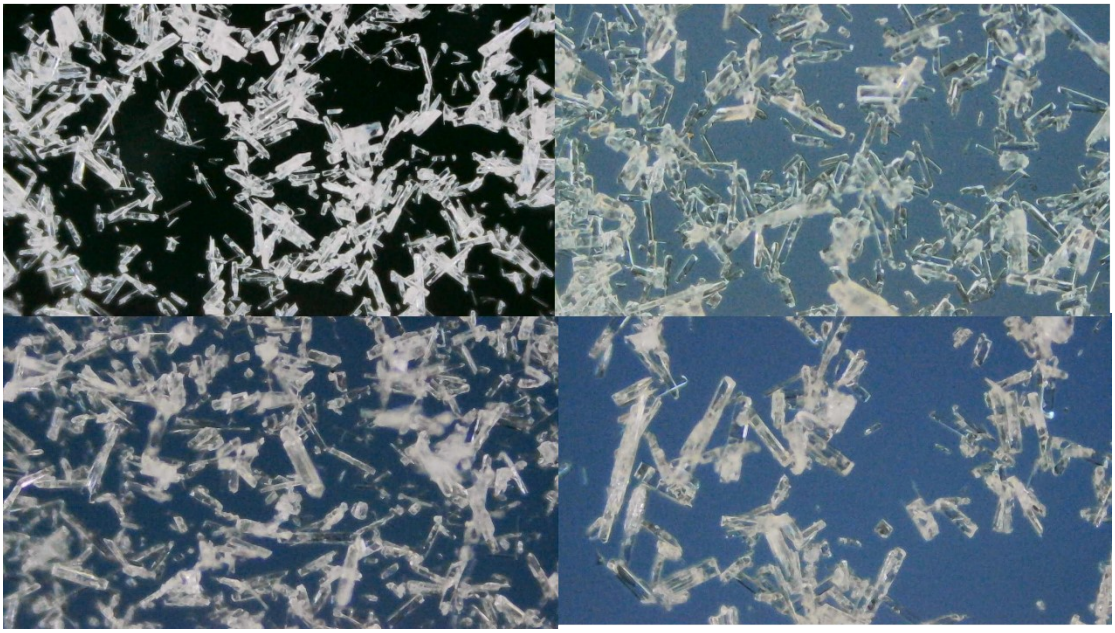

Fig. S2. Optical microscope images of pure rod-shaped **ZrP-3** crystals at different magnifications.

Section S5. SEM-EDS analysis

Scanning electron microscopy images and energy-dispersive spectroscopy data were recorded on an FEI Quanta 200FEG Scanning Electron Microscope with the energy of the electron beam being 30 keV.

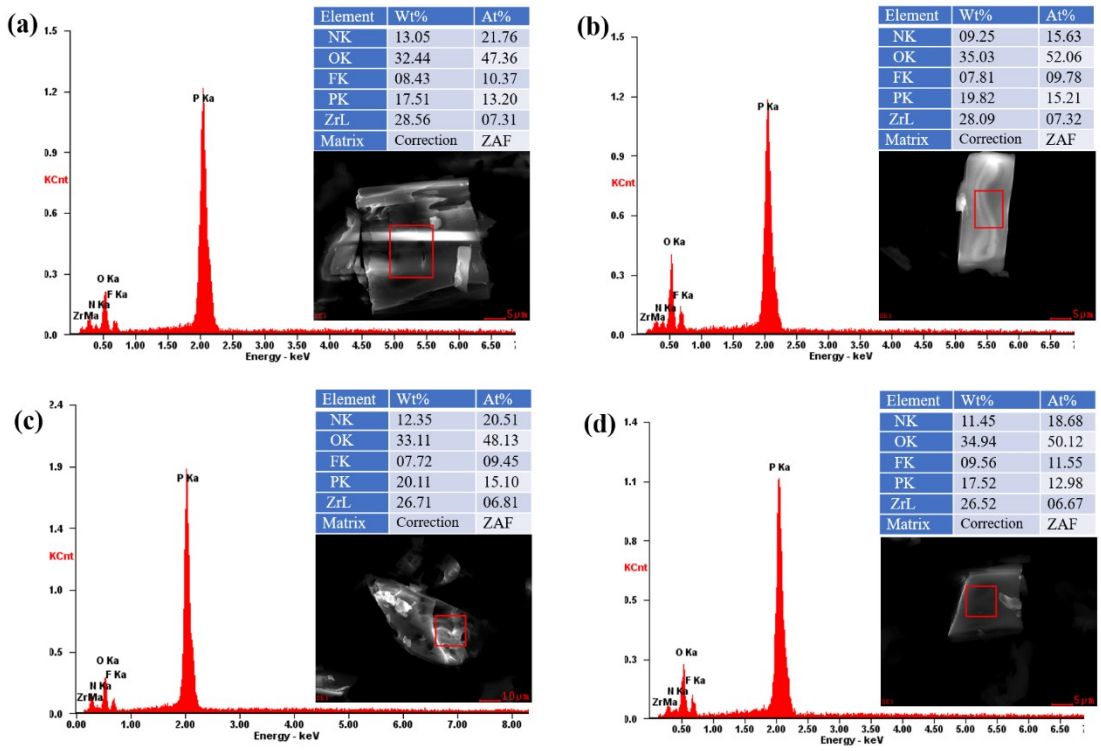

Fig. S3. SEM and EDS analysis of **ZrP-3.**

Section S6. FT-IR spectrum

The ATR/FTIR spectra of the sample without KBr were recorded in the range of 4000-400 cm^{-1} by a Thermo Scientific Nicolet iS50 spectrometer.

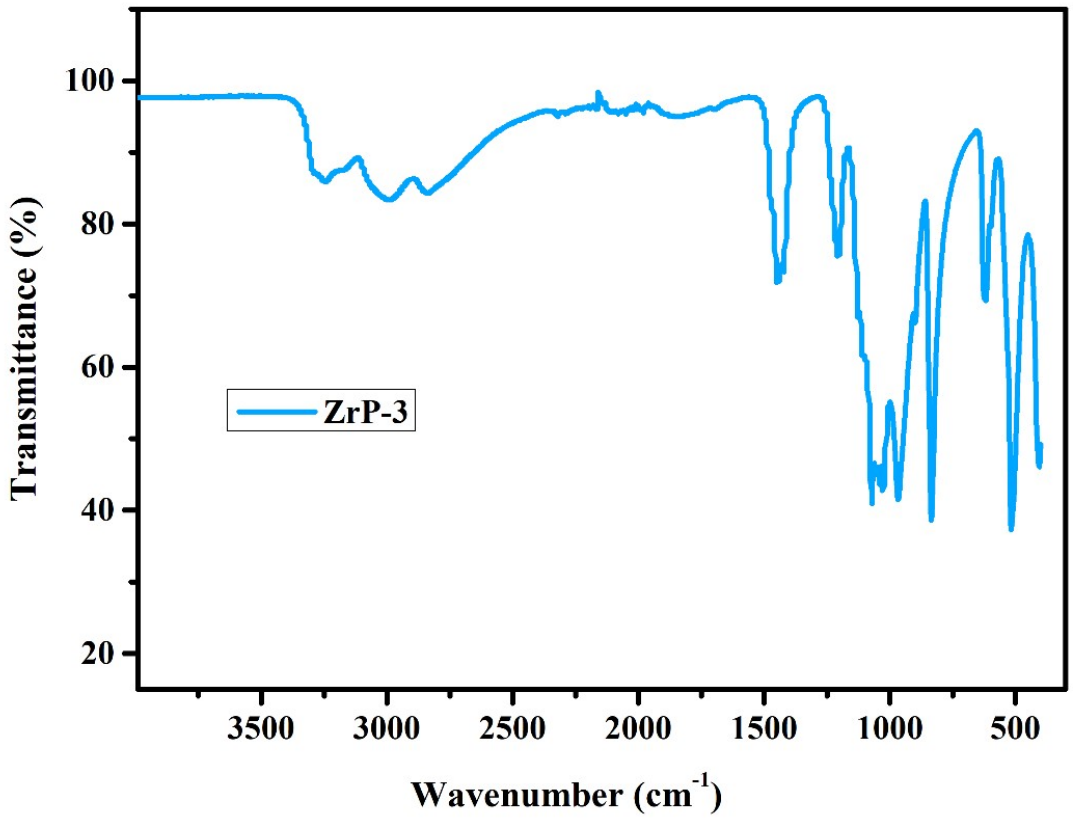

Fig. S4. FT-IR spectra of **ZrP-3.**

Section S7. Proton conductivity measurements and durability test

Alternating current impedance measurements were carried out on a Solartron SI 1260 Impedance/Gain-Phase Analyzer with an applied ac voltage amplitude of 500 mV over a frequency range of 5 MHz to 1 Hz. A bulk crystalline powder was compressed into a pellet with 1000 kg of pressure, the diameter of the pellet was 3 mm, and the thickness ranged from 1~2 mm.

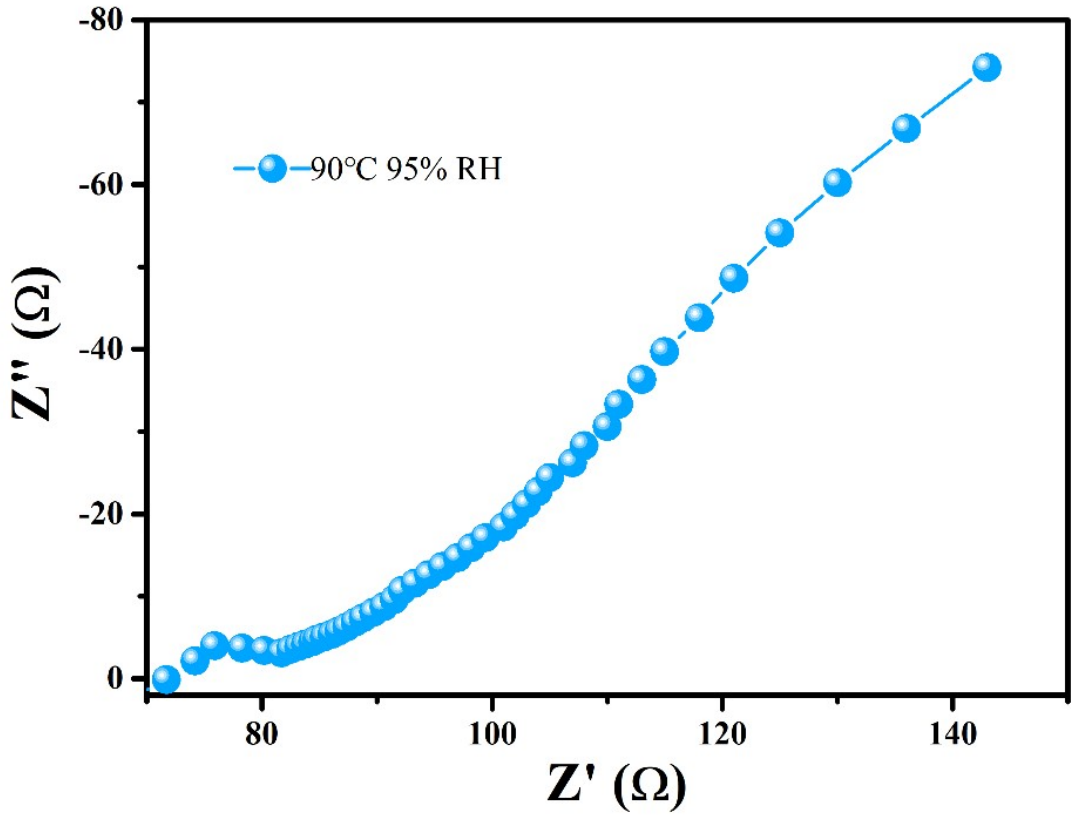

Fig. S5. Impedance spectrum of **ZrP-3** under 95% RH and 90 ℃.

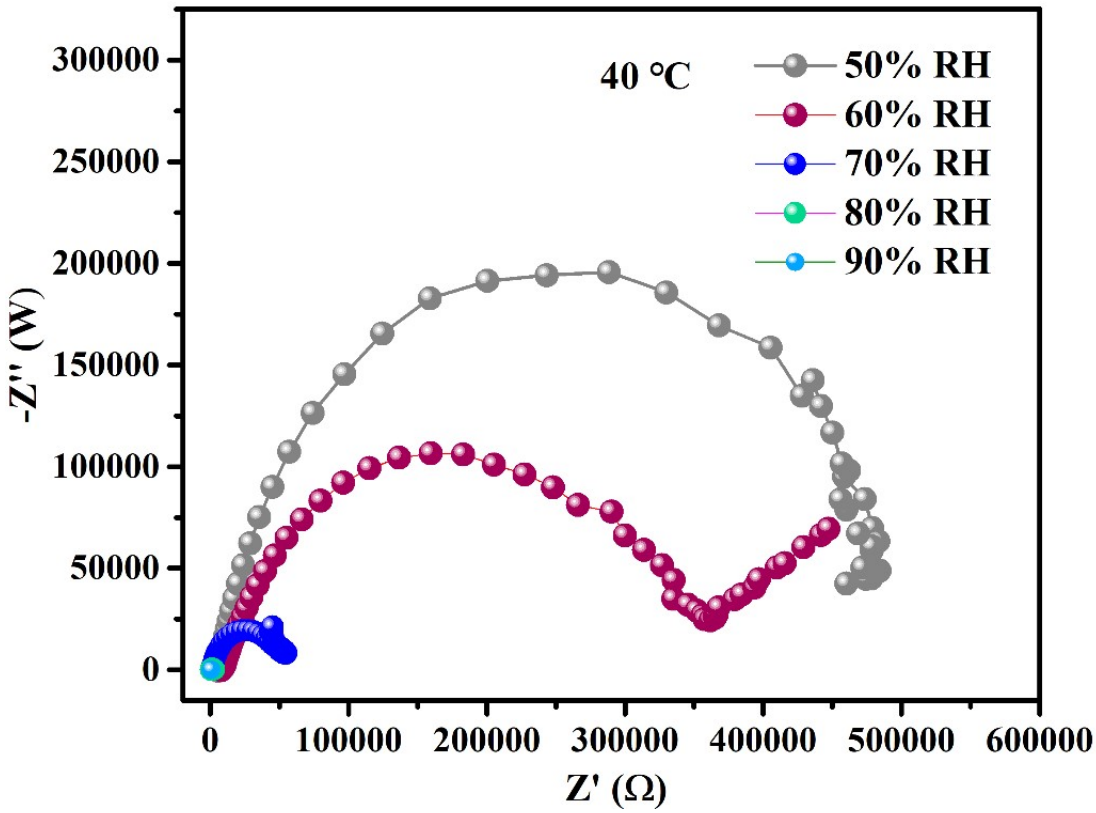

Fig. S6. Impedance spectrum of **ZrP-3** at different relative humidity (50%-90%RH) under 40°C.

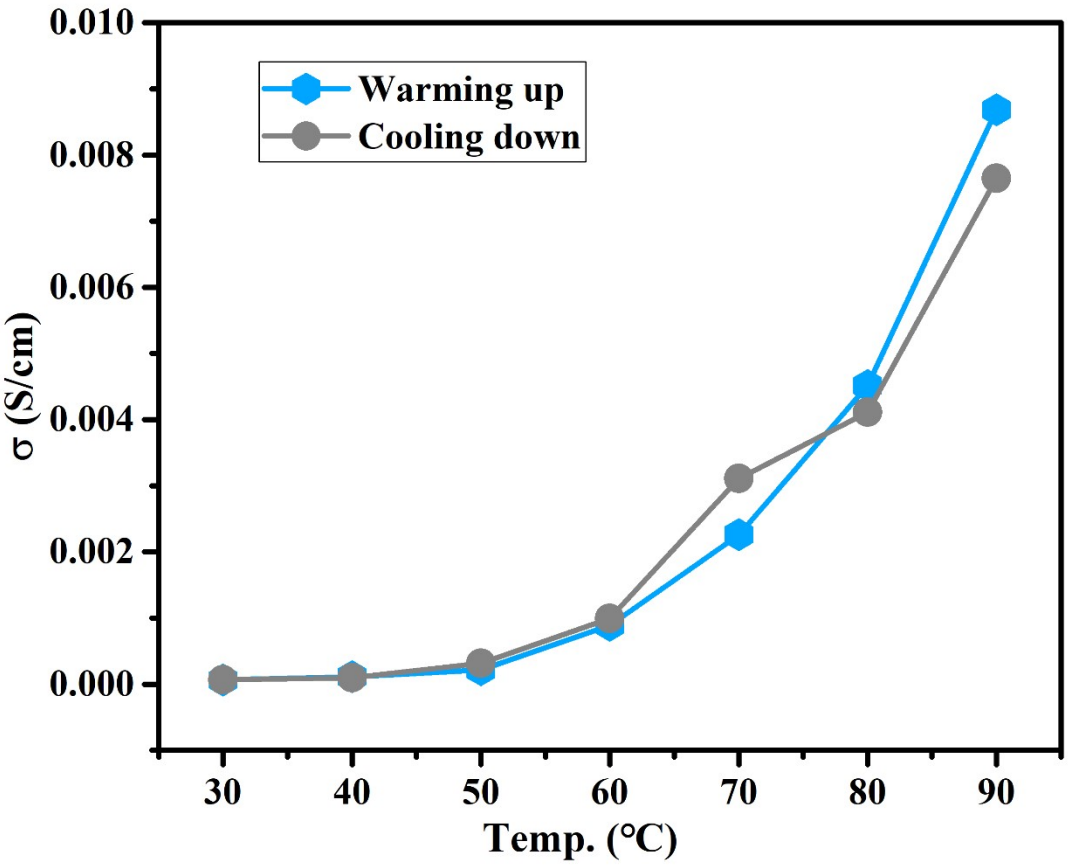

Fig. S7. Cyclic test of proton conductivity with temperature (90%RH).