Electronic Supplementary Information

Post-synthesis Functionalization of ZIF-90 with Sulfonate Groups for High Proton Conduction

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Experimental details

Materials and Reagents

All chemicals and solvents obtained from suppliers were used without further purification. All solvents were analytical grade reagent.

Synthesis of ZIF-90

The synthesis of ZIF-90 is based on the method reported in the literature with a slight modification.[S1] The imidazole-2-carbaldehyde (H-ICA, 0.70 g, 7.19 mmol) was dissolved in 30 mL of methanol, and then the triethylamine (1 mL, 7.19 mmol) was added into the solution. The resulting solution was stirred at room temperature for 5 minutes. Subsequently, a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.07 g, 3.59 mmol) in methanol (30 mL) was added, and the mixture was stirred at 70 °C for 30 min. After the reaction was completed, it was naturally cooled to room temperature, filtered, and washed with methanol several times. The pristine sample was placed in a blast drying oven at 60 °C for 12 h to obtain a white powder of ZIF-90.Elemental analyses (%): Calcd C, 38.61; N, 16.07; H, 2.90.

Synthesis of ZIF-90-$SO_3Na_{(2.3)}$

Firstly, a saturated solution of sodium bisulfite was prepared. Next, ZIF-90 (0.10 g, 0.39 mmol/-CHO) was added to methanol (20 mL) in a round bottom flask, followed by a quick addition of saturated sodium bisulfite solution (0.11 mL, 1.56 mmol). The reaction system was refluxed at 60 °C for 24 h, cooled to room temperature naturally, filtered, and washed with methanol for several times. The obtained sample was treated

in a blast drying oven at 60 °C for 12 h to obtain a milky white powder of ZIF-90-$SO_3Na_{(2.3)}$. Elemental analyses (%): Calcd C, 33.78; N, 14.56; H, 2.48; S, 2.29.

Instrumentation

Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku (Japan)/SmartLab (9kW) rotating target X-ray diffractometer with Cu sealed tub (λ=1.54178 Å). The thermal gravimetric analysis (TGA) was performed on a TA Q50 instrument from TA Company of the USA under the condition of the test is the N_2 atmosphere, the heating rate of 10 °C/min, and a temperature range of from room temperature to 800 °C. Fourier transform infrared spectroscopy (FT-IR) measurements were performed using the Bucks HP9 2FX infrared spectrometer in the wavelength range of 4000 to 400 cm^{-1}. The surface of the composite was observed using a scanning electron microscope (SEM, Merlin Compact). Elemental analysis (EA) was performed using a FLASH 2000 organic elemental analyzer. The inductively coupled plasma (ICP) experiments were conducted in an ICP-OES: Aglient 5110 device.

Measurements of proton conductivity

All AC impedance tests were measured using the RST5200F electrochemical workstation. Proton conductivity was studied at different temperatures and relative humidity (RH) using AC impedance spectroscopy. The RH was controlled by using different saturated aqueous salt solutions: potassium iodide (68% RH), Sodium chloride (75% RH), potassium chloride (85% RH), potassium nitrate (93% RH), and potassium sulfate (98% RH). The samples were ground and pressed into a piece under a pressure

of 4 ~ 5 MPa, and the thickness of the particles was measured to be 0.9 ~ 1.3 mm using a vernier caliper, clamped with a copper (99.9%) electrode and fully hydrated at various relative humidity for at least 24 hours, and then conductivity measurements were made under various relative humidity conditions. Collect the AC impedance spectrum of the sample by using an AC voltage of 100 mV and an AC frequency of 100 Hz ~ 1.39 MHz. Impedance plots were fitted by ZSimpWin software. The conductivity is calculated using eq 1[S2]:

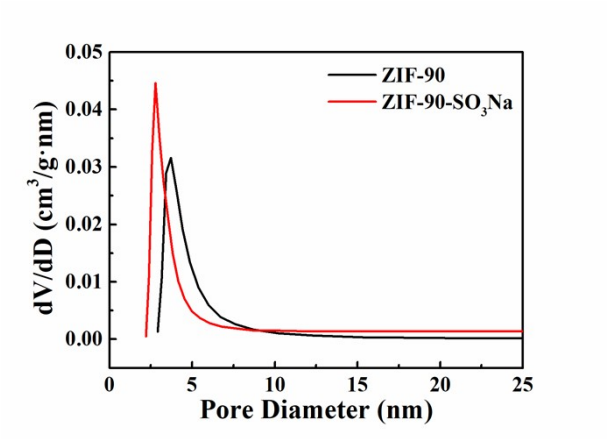
$$\sigma = L/AR \tag{1}$$

where σ is the proton conductivity (S cm^{-1}), R is the impedance value, L is the effective thickness (cm) of the sample, and A is the effective cross-sectional area (cm^2) of the sample.

The activation energy (E_a) is calculated by eq 2[S3]:

$$\ln(\sigma T) = lnA - \frac{E_a}{k_B T} \tag{2}$$

where the symbol σ is the proton conductivity, E_a represents the proton transport activation energy, k_B is the Boltzmann constant, and A is the pre-exponential factor, and T is the temperature.



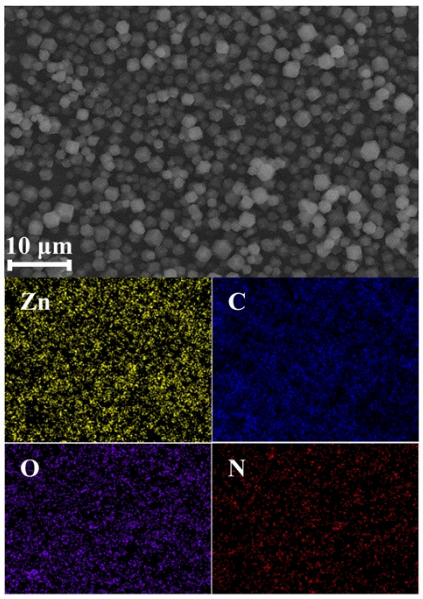


Figure S1. Pore size distribution curves of ZIF-90 and ZIF-90-$SO_3Na_{(2.3)}$.

Figure S2. Scanning electron microscope and EDS maps images of ZIF-90.

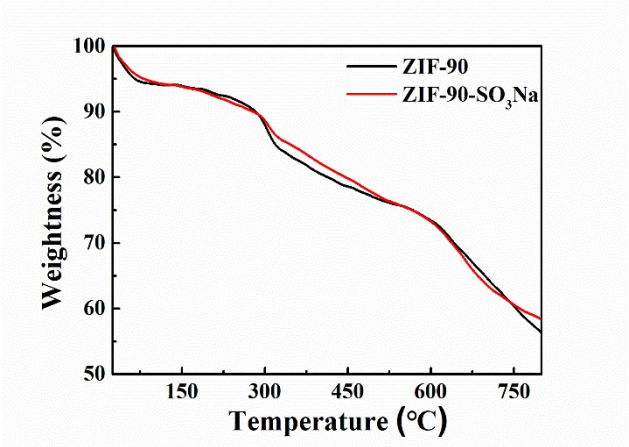


Figure S3. TGA curves of the ZIF-90 and ZIF-90-$SO_3Na_{(2.3)}$.

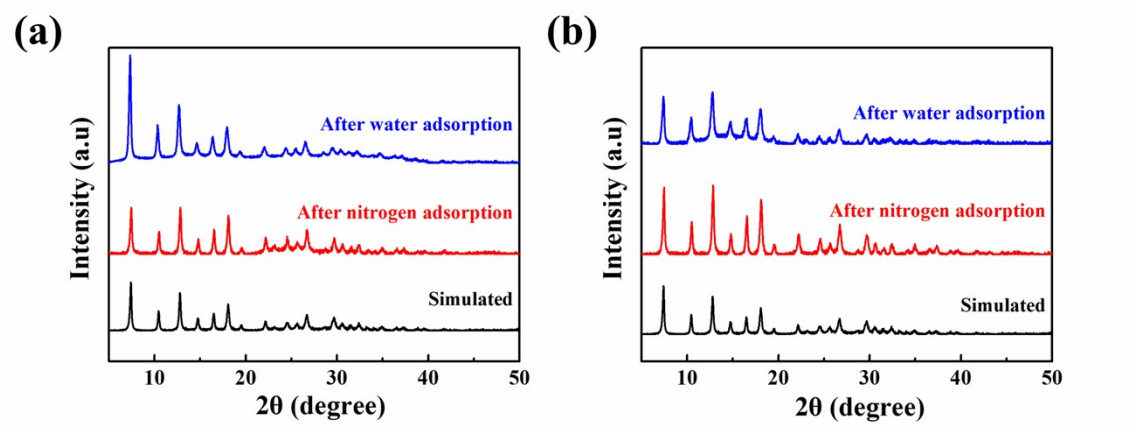


Figure S4. Powder X-ray diffraction patterns of (a) ZIF-90 and (b) ZIF-90-$SO_3Na_{(2.3)}$ after N_2 and water vapor adsorption-desorption measurements.

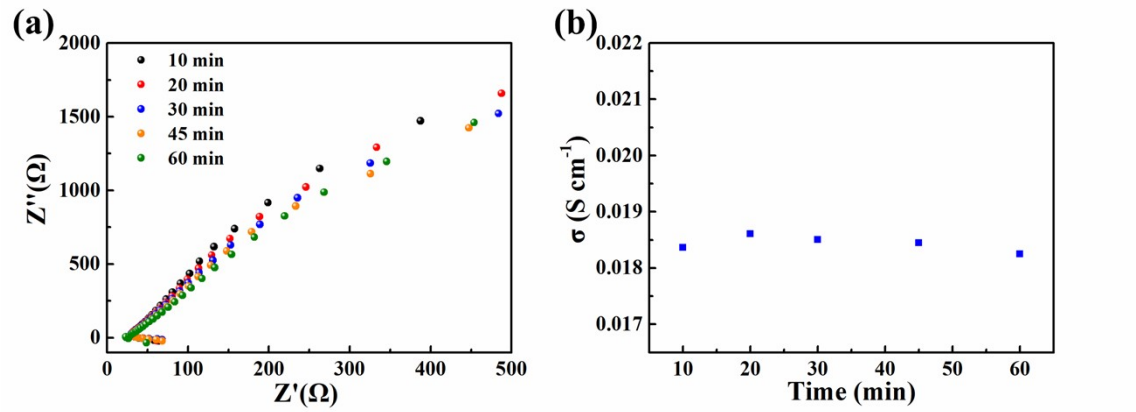


Figure S5. (a) Nyquist plot and (b) time-dependent conductivity plot of ZIF-90-$SO_3Na_{(2.3)}$ at 100 °C and 93% RH.

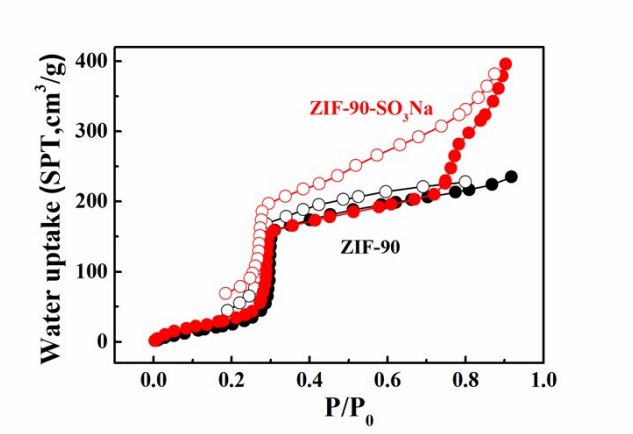


Figure S6. The water adsorption and desorption isotherm of ZIF-90 and ZIF-90-$SO_3Na_{(2.3)}$. (All tests were conducted at 25°C. Filled and open symbols represent adsorption and desorption, respectively.)

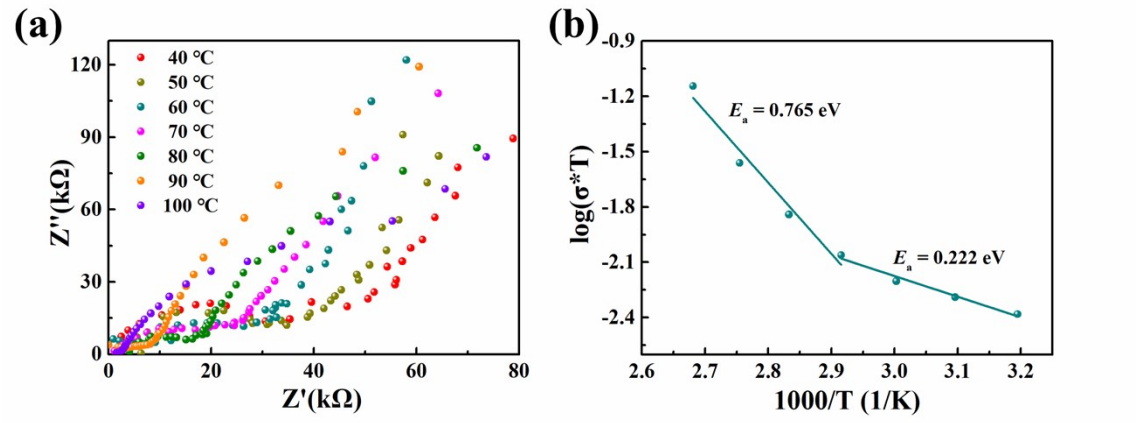


Figure S7. (a) Temperature dependence of Nyquist plot for ZIF-90 at 98% RH; (b) corresponding Arrhenius curve.

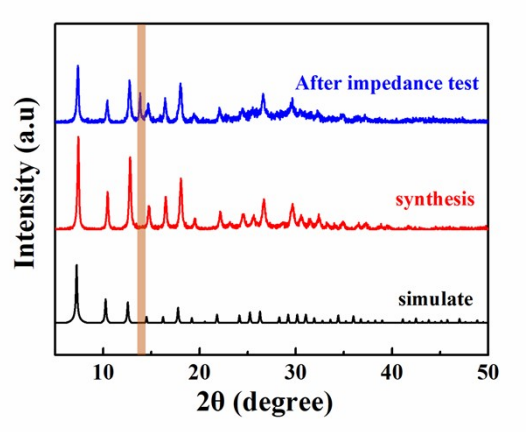


Figure S8. Powder X-ray diffraction pattern of ZIF-90 sample after AC impendence measurement at 98% RH.

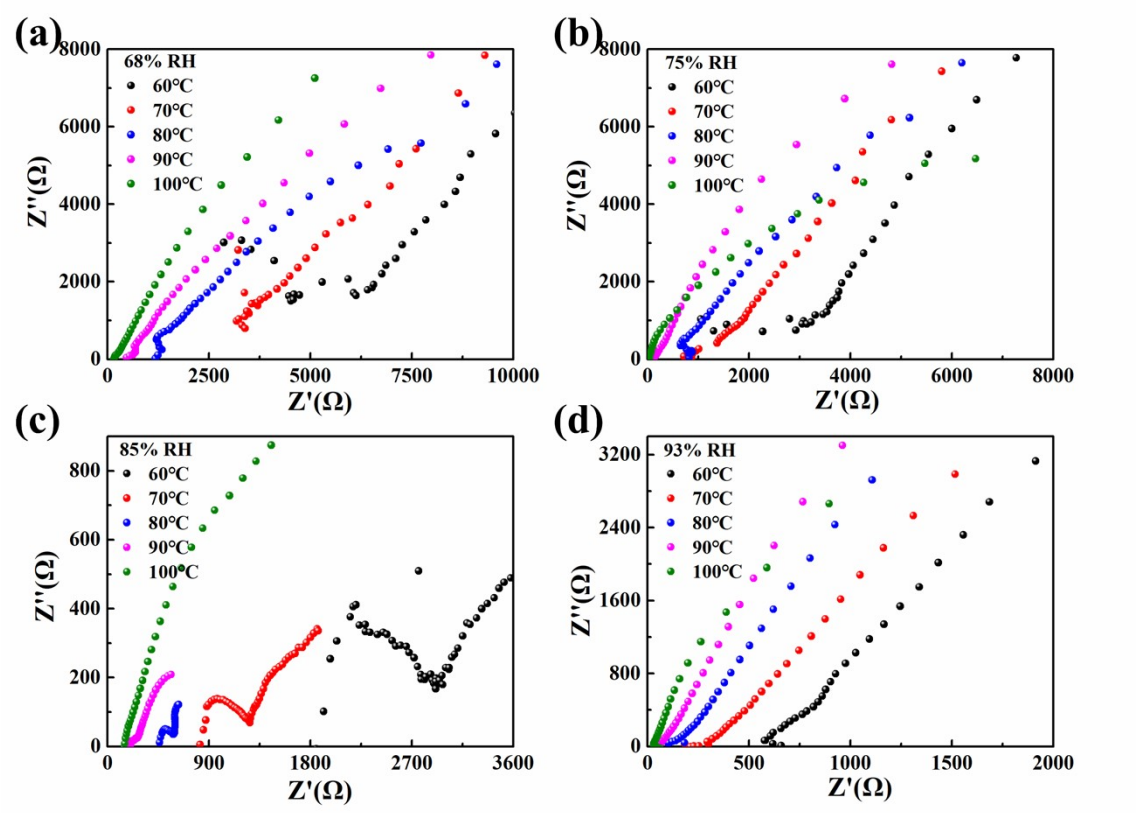


Figure S9. Temperature dependence of Nyquist plot for ZIF-90-$SO_3Na_{(2.3)}$ at (a) 68% RH, (b) 75% RH, (c) 85% RH, and (d) 93% RH.

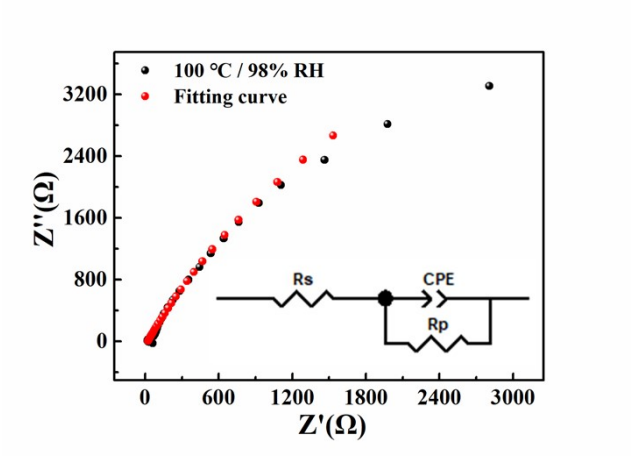


Figure S10. Nyquist plot of ZIF-90-$SO_3Na_{(2.3)}$ measured at 100°C and 98% RH (black) and its fitting curve (red). The inserted diagram provides an equivalent circuit diagram for analyzing the Nyquist plot diagram.

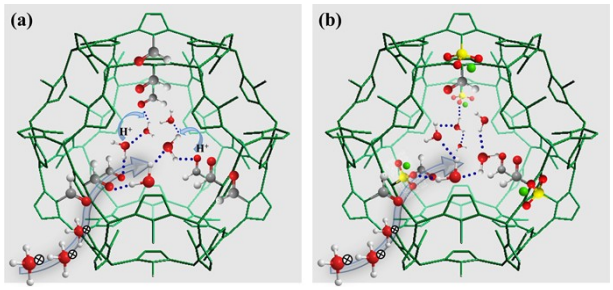


Figure S11. Diagram of the proton conduction path in ZIF-90 (a) and ZIF-90-$SO_3Na_{(2.3)}$ (b) under high-humidity conditions.

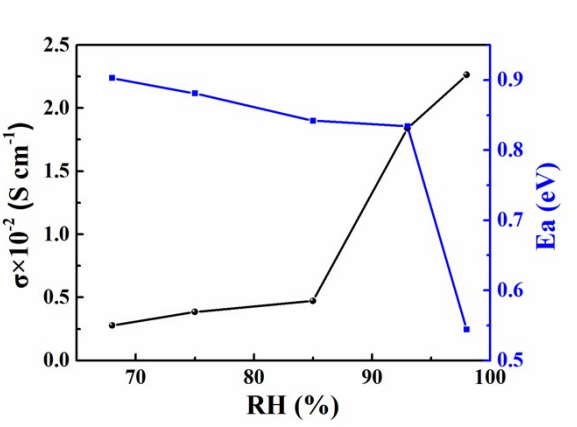


Figure S12. Proton conductivity at 100 °C and activation energy (E_a) at different relative humidity (RH) of ZIF-90-$SO_3Na_{(2.3)}$.

Table S1. σ values (S cm^{-1}) of ZIF-90-$SO_3Na_{(2.3)}$ at various RHs and temperatures

RH (%)	60 ℃	70 ℃	80 ℃	90 ℃	100 ℃
68	1.07×10^{-4}	1.91×10^{-4}	4.50×10^{-4}	1.03×10^{-3}	2.77×10^{-3}
75	1.83×10^{-4}	3.21×10^{-4}	7.75×10^{-4}	2.10×10^{-3}	3.84×10^{-3}
85	2.36×10^{-4}	5.45×10^{-4}	1.18×10^{-3}	2.71×10^{-3}	4.72×10^{-3}
93	9.26×10^{-4}	1.91×10^{-3}	4.64×10^{-3}	9.00×10^{-3}	1.84×10^{-2}
98	3.33×10^{-3}	5.54×10^{-3}	8.69×10^{-3}	1.47×10^{-2}	2.26×10^{-2}

References

S1 P. F. Liguori, B. Russo, A. Melicchio and G. Golemme, *New J. Chem.*, 2017, **41**, 13235-13239.

S2 S.-Z. Huang, S.-S. Liu, H.-J. Zhang, Z. Han, G. Zhao, X.-Y. Dong and S.-Q. Zang, *Acs Appl. Mater. Interfaces*, 2020, **12**, 28720-28726.

S3 S.-S. Liu, Z. Han, J.-S. Yang, S.-Z. Huang, X.-Y. Dong and S.-Q. Zang, *Inorg. Chem.*, 2020, **59**, 396-402.