Enhanced Proton Conductivity in Cu-BTC Thin-Film Membrane through Lysine Incorporation and mixed matrix membrane

Yuan Gao,[a] Bo Liu,[a] Hanlu Xu,[a] Caixia Shi,[a] Ning Yan,[b] Shaorong Wang,[*a] Rongli Jiang[*a]

School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu, 221116, China.

School of Physics and Technology, Wuhan University, Wuhan, Hubei, 430072, China.

Experimental

Characterizations

Fourier Transform Infrared Spectroscopy (FTIR) was carried out on KBr pellets using a NICOLET i5 Fourier Transform Infrared Spectrometer, with a measurement range of 4000 - 450 cm^{-1} and a spectral resolution of 0.4 cm^{-1}. PXRD analysis was performed on a Bruker AXS D8 ADVANCE X-ray diffractometer, using a copper target X-ray generator, with the scanning range being 5-60°, working voltage of 60 kV, and maximum output power of 3 KW. Thermal analysis was conducted using TGA and differential scanning calorimetry (DSC) on a NETZSCH Jupiter® STA 449F3 instrument, in air (20 mL min^{-1}), at a speed of 10 K min^{-1}, and over a temperature range of 35 - 800 °C. X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition and surface states of the materials, using a Thermo Fisher spectrometer (ESCALAB 250Xi, Thermo Fisher, USA) and monochromatized Al Ka radiation (hv = 1486.6 eV).

The AC impedance spectra were measured using the CHI electrochemical workstation, with the samples prepared as pellets of uniform particle size, typically 0.4 mm (0.05 mm thickness), using a press and a 13 mm diameter die. The pellets were sandwiched between parallel copper plates and clamped in a humidity environment controlled by different saturated salt solutions ($Zn(NO_3)_2$, $MgCl_2$, $CoCl_2$, KBr, KNO_3). The impedance analysis was performed using the two-point method at various temperatures (30 - 80 °C) and relative humidity (20 - 100% RH), with the AC impedance value S obtained after fitting the obtained data. The proton conductivity value (σ) was calculated using the following formula:

$$\sigma = L/(S \times A)$$

Where L is the thickness of the sample (cm), A is the surface area (cm^2), S is the impedance, δ is the proton conductivity (S cm^{-1}).

The activation energy (E_a) is calculated based on Arrhenius equation:

$$\ln(\sigma T) = \ln A - E_a/RT$$

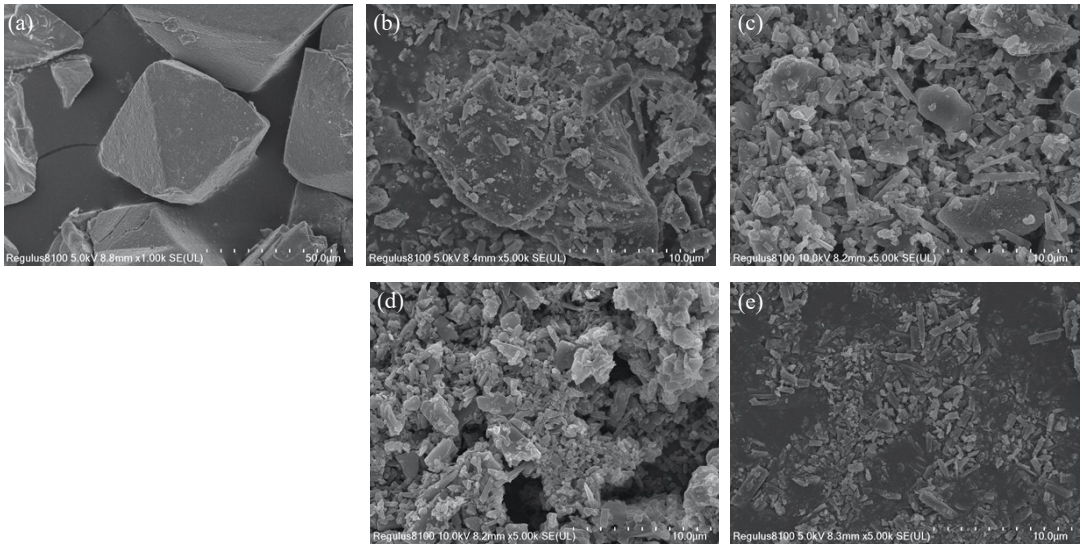

Fig. S1 SEM images of (a) Cu-BTC, (b) Cu-BTC-Lys (10 wt%), (c) Cu-BTC-Lys (20 wt%), (d) Cu-BTC-Lys (30 wt%), and (e) Cu-BTC-Lys (40 wt%)

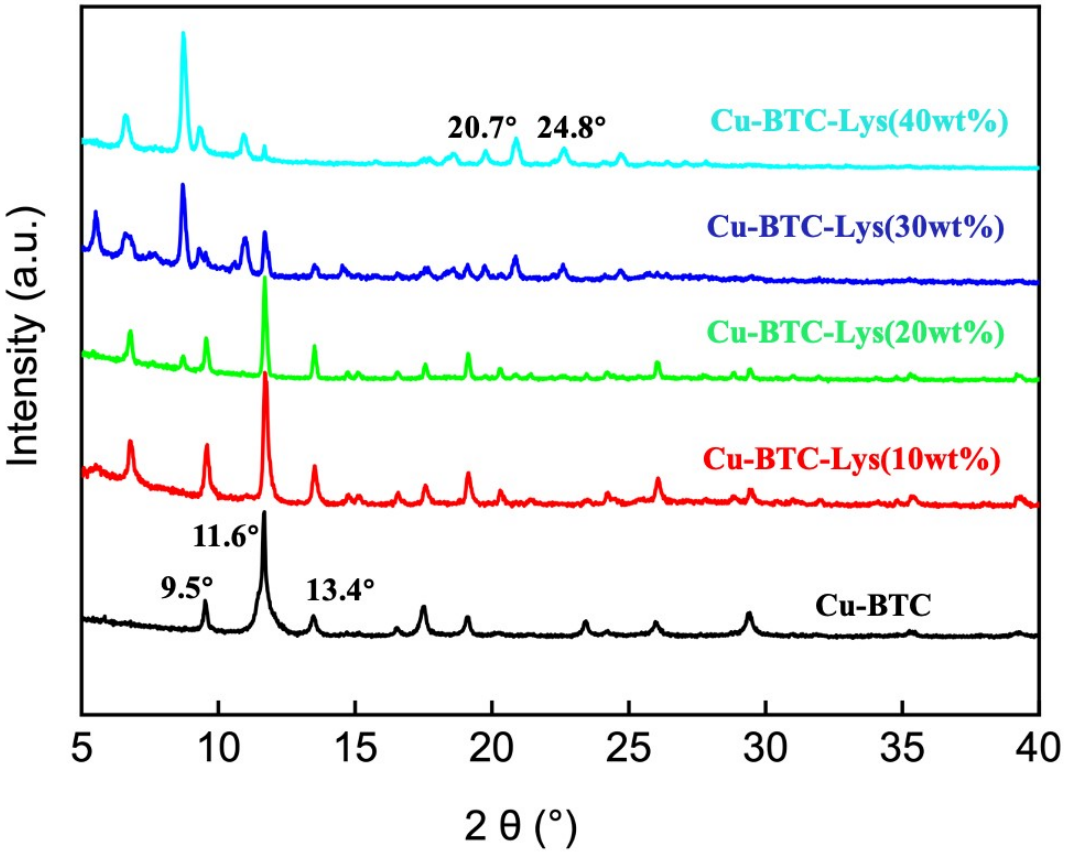

Fig. S2 PXRD spectra of Cu-BTC-Lys placed in water atmosphere for 1 day.

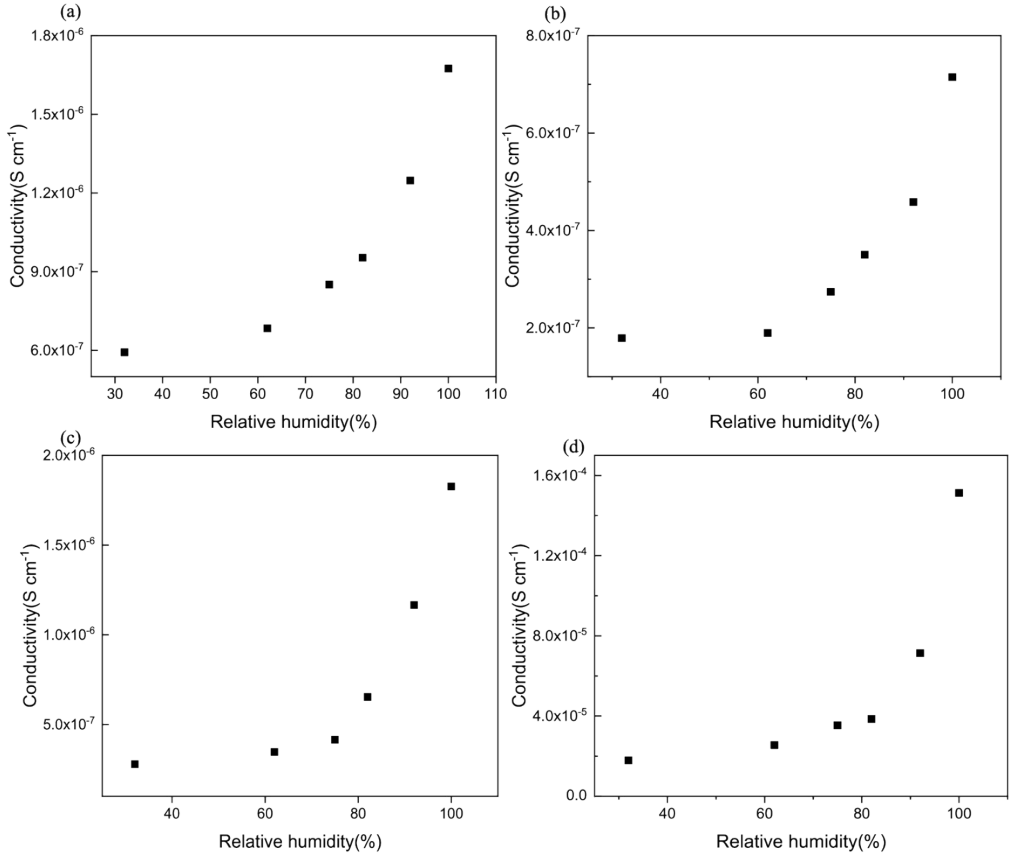

Fig. S3 The proton conductivity of (a) Cu-BTC-Lys (10 wt%), (b) Cu-BTC-Lys (20 wt%), (c) Cu-BTC-Lys (30 wt%), and (d) Cu-BTC-Lys (40 wt%) measured at 25 °C and under different relative humilities (32%, 62%, 75%, 82%, 92% and 100%).

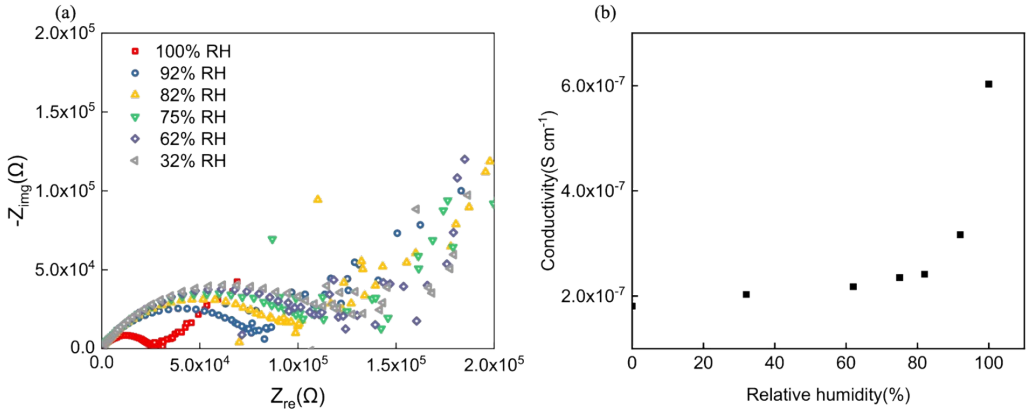

Fig. S4 The Nyquist plot (a) the proton conductivity (b) of pristine Cu-BTC measured at 25 °C under different relative humilities (32%, 62%, 75%, 82%, 92% and 100%).

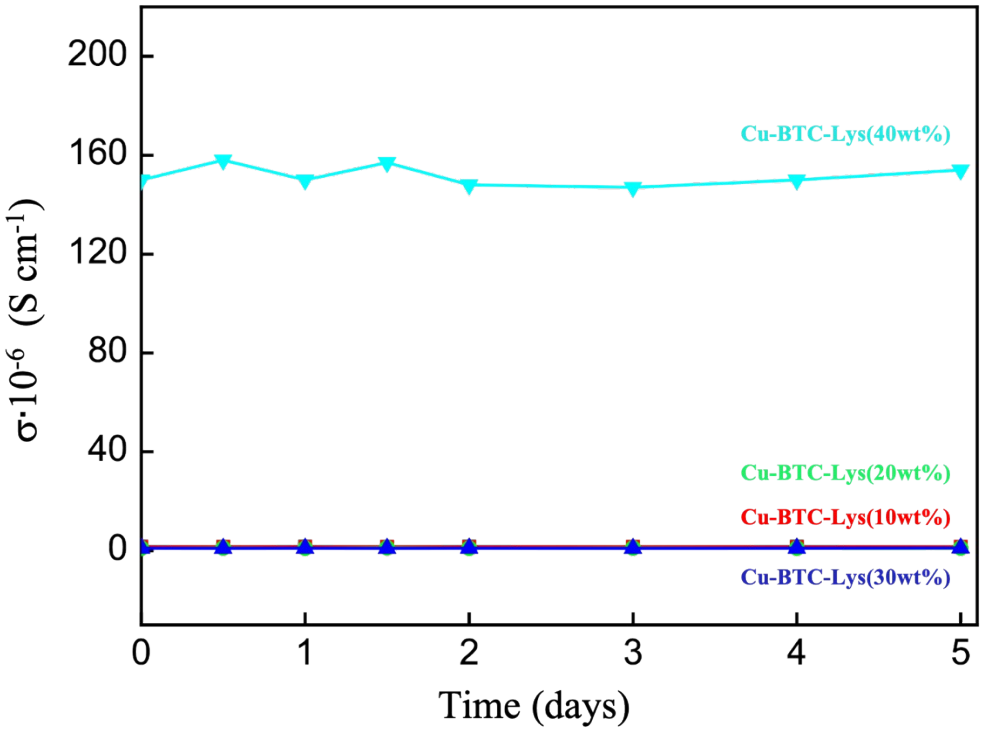

Fig. S5 Time-dependent proton conductivity of Cu-BTC-Lys measured under 100% RH and 80 °C.

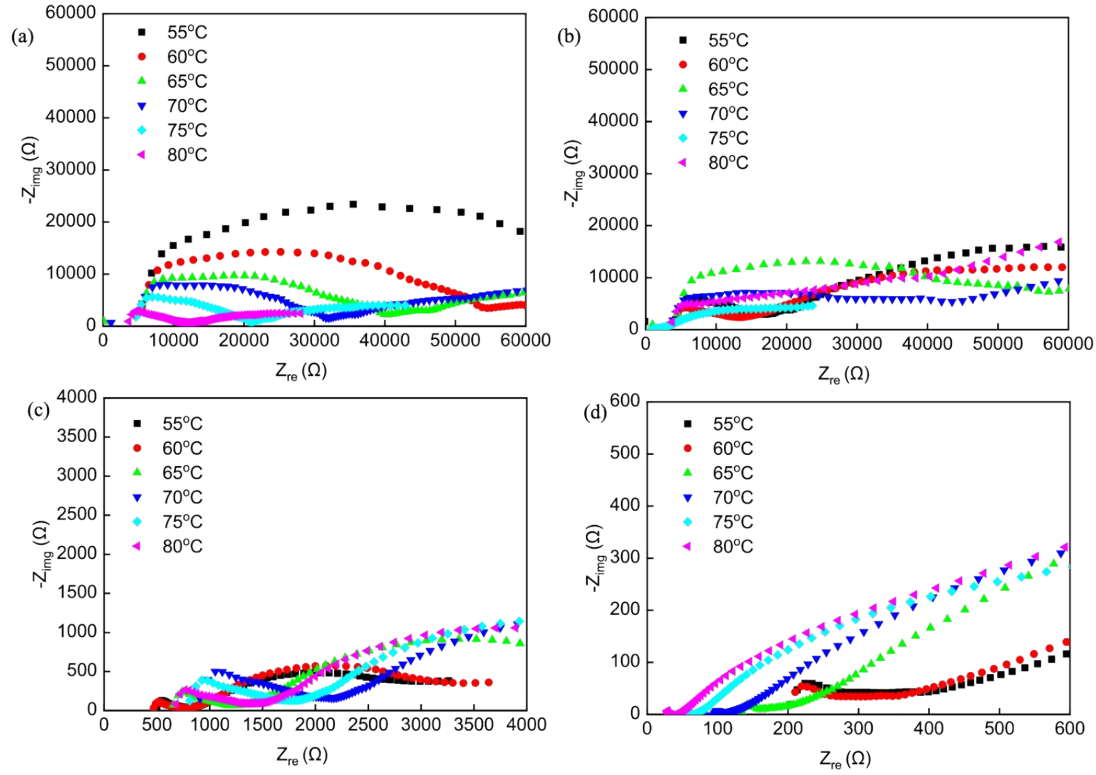

Fig. S6 Nyquist plot of (a) Cu-BTC-Lys (10 wt%), (b) Cu-BTC-Lys (20 wt%), (c) Cu-BTC-Lys (30 wt%), and (d) Cu-BTC-Lys (40 wt%) measured at 100% RH and under different temperatures (55 °C, 60 °C, 65 °C, 70 °C, 75 °C, and 80 °C).

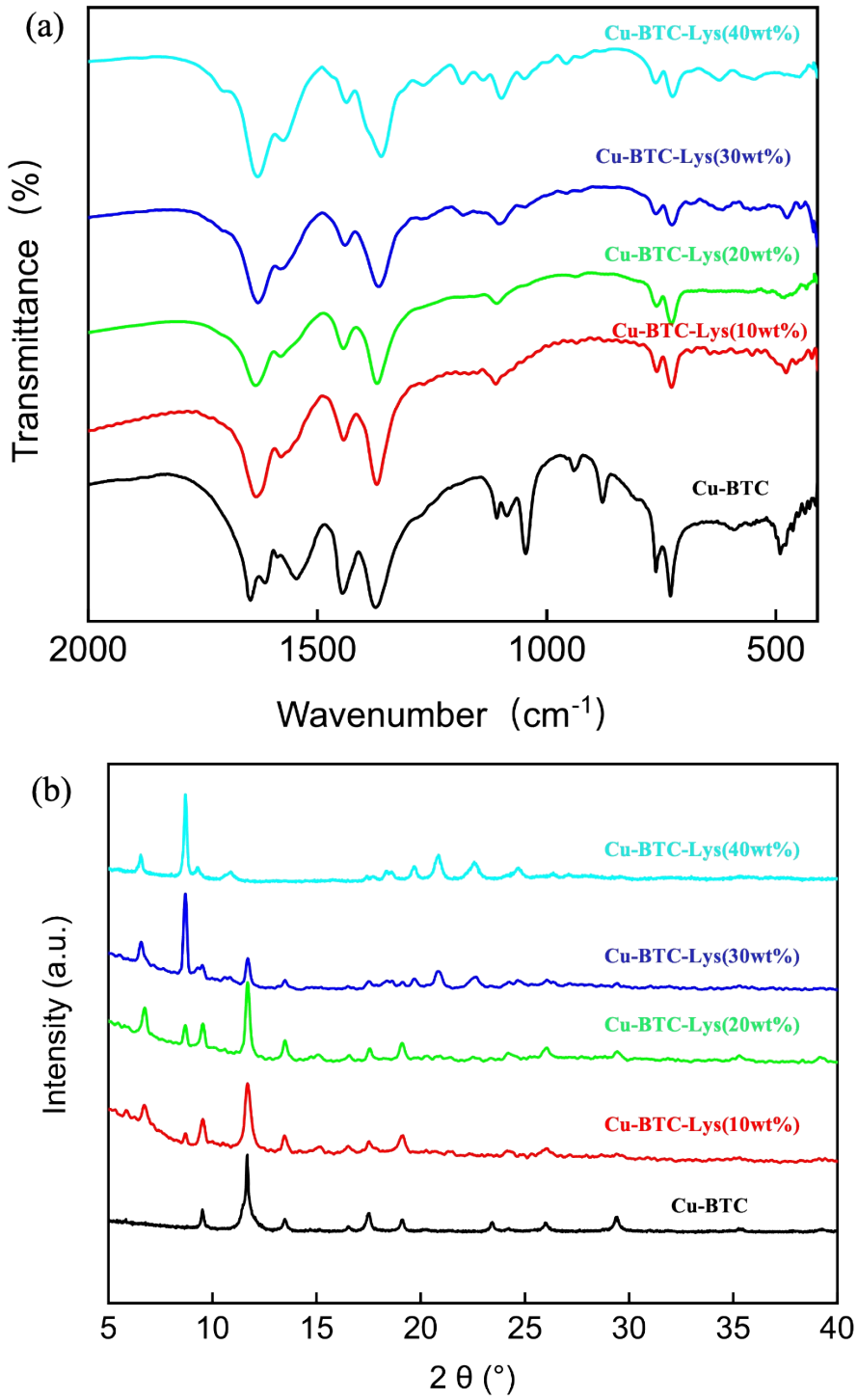

Fig. S7 FTIR (a) and PXRD (b) spectra of Cu-BTC-Lys (40 wt%) after proton conductivity measurements.

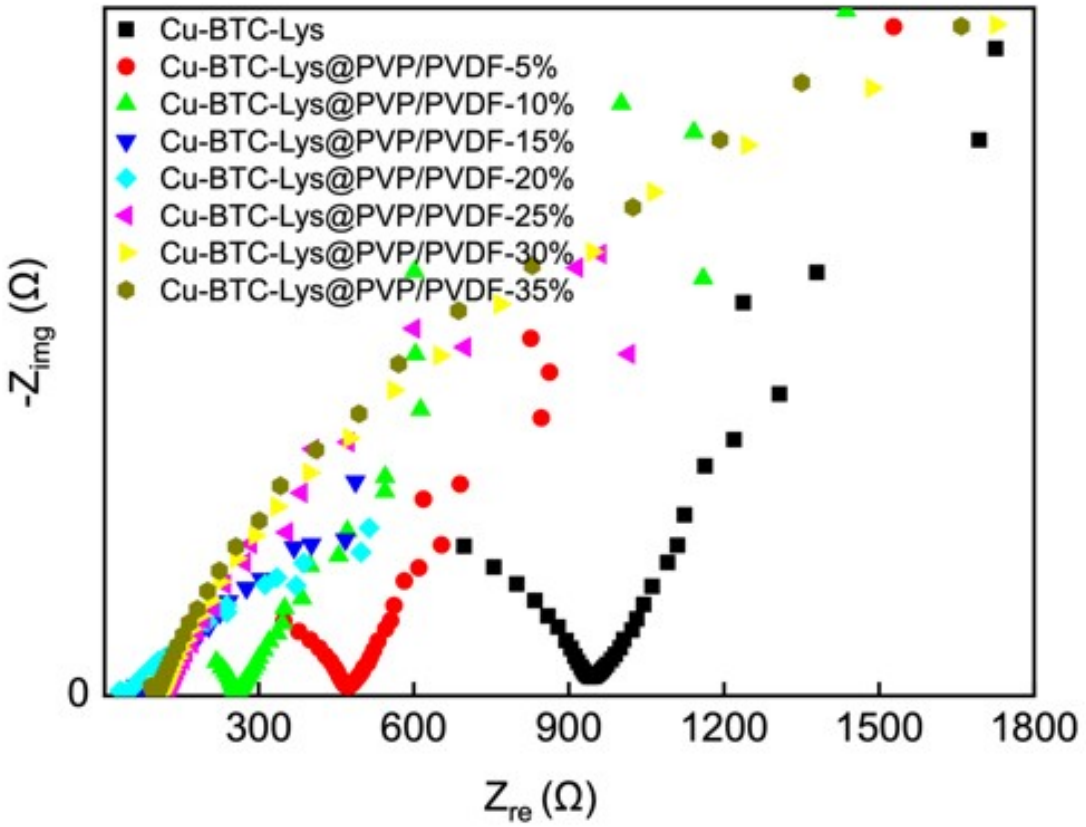

Fig. S8 Nyquist plot of Cu-BTC-Lys, Cu-BTC-Lys@PVP/PVDF-5, Cu-BTC-Lys@PVP/PVDF-10, Cu-BTC-Lys@PVP/PVDF-15, Cu-BTC-Lys@PVP/PVDF-20, Cu-BTC-Lys@PVP/PVDF-25, Cu-BTC-Lys@PVP/PVDF-30, and Cu-BTC-Lys@PVP/PVDF-35 membranes measured at 25 °C and 100% RH.

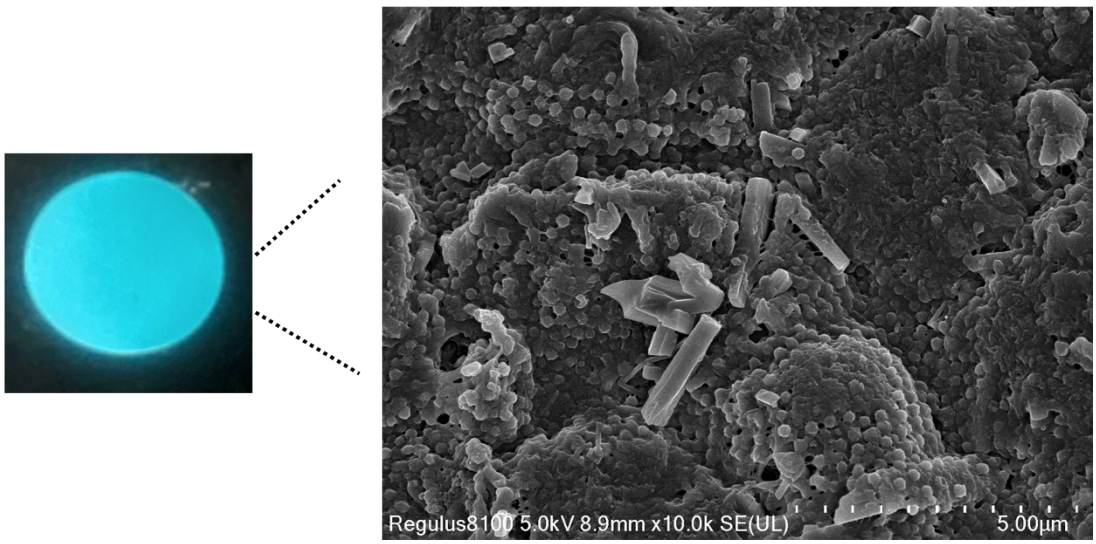

Fig. S9 The optical (left) and SEM (right) images of Cu-BTC-Lys@PVP/PVDF-20

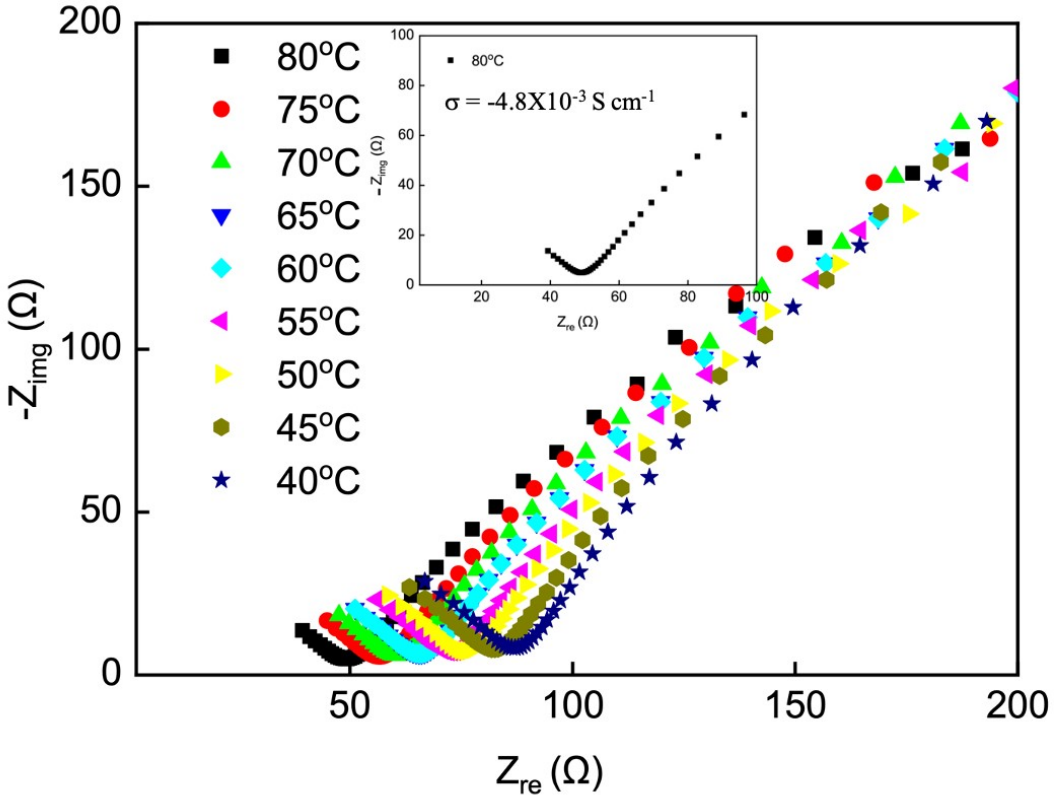

Fig S10 Nyquist plot of Cu-BTC-Lys@PVP/PVDF-20 measured at 100% RH and under different temperatures (40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, and 80 °C). The inset shows a magnified view of the Nyquist plot specifically at 80 °C.

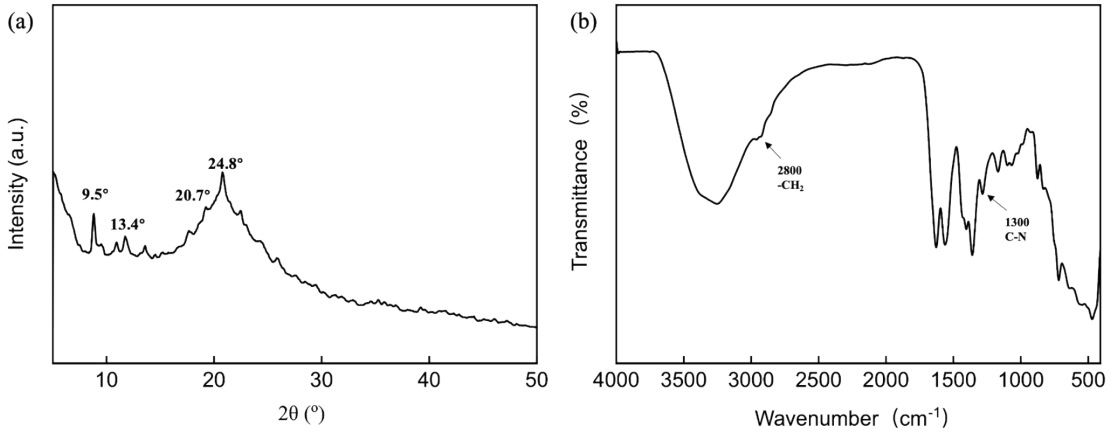

Fig S11 FTIR (a) and PXRD (b) spectra of Cu-BTC-Lys@PVP/PVDF-20 after proton conductivity measurements.

Table S1 Performance indicators for PVP/PVDF based proton-conducting MOFs membranes

Compound	Conductivity (S cm^{-1})	Activation energy (eV)	Measurement condition	Reference
Cu-MOF@PVP/PVDF-50	4.36×10^{-4}	0.09	80 °C, 98% RH	1
Fe^{III}-MOF@PVP/PVDF	1.77×10^{-3}	0.15	80 °C,9 8% RH	2
Cu-SAT@PVP/PVDF	0.80×10^{-3}	0.187	80 °C, 98% RH	3
BMIM-OH/ZIF@PVP/PVDF	1.02×10^{-3}	0.15	80 °C, 98% RH	4
SIB-3@PVP/PVDF	4.3×10^{-3}	0.09	50° C, 23% RH	5
MOF-801@PVP/PVDF-60	1.84×10^{-3}	Not mentioned	60 °C, 98% RH	6
Cu-BTC-Lys@PVP/PVDF	4.8×10^{-3}	0.15	80 °C, 98% RH	This work

1. Bao, Y.-L.; Zheng, J.-Y.; Zheng, H.-P.; Qi, G.-D.; An, J.-R.; Wu, Y.-P.; Liu, Y.-L.; Dong, W.-W.; Zhao, J.; Li, D.-S., Cu-MOF@PVP/PVDF hybrid composites as tunable proton-conducting materials. *Journal of Solid State Chemistry* **2022,** *310*, 123070.

2. Wen, T.; Shao, Z.; Wang, H.; Zhao, Y.; Cui, Y.; Hou, H., Enhancement of Proton Conductivity in Fe-Metal–Organic Frameworks by Postsynthetic Oxidation and High-Performance Hybrid Membranes with Low Acidity. *Inorganic Chemistry* **2021,** *60* (24), 18889-18898.

3. Moi, R.; Ghorai, A.; Banerjee, S.; Biradha, K., Amino-and sulfonate-functionalized metal–organic framework for fabrication of proton exchange membranes with improved proton conductivity. *Crystal Growth & Design* **2020,** *20* (8), 5557-5563.

4. Zhang, T.; Yu, G.; Liang, X.; Zhao, N.; Zhang, F.; Qu, F., Development of anion conducting zeolitic imidazolate framework bottle around ship incorporated with ionic liquids. *International Journal of Hydrogen Energy* **2019,** *44* (29), 14481-14492.

5. Du, J.; Yu, G.; Lin, H.; Jie, P.; Zhang, F.; Qu, F.; Wen, C.; Feng, L.; Liang, X., Enhanced proton conductivity of metal organic framework at low humidity by improvement in water retention. *Journal of colloid and interface science* **2020,** *573*, 360-369.

6. Zhang, J.; Bai, H.-J.; Ren, Q.; Luo, H.-B.; Ren, X.-M.; Tian, Z.-F.; Lu, S., Extra water-and acid-stable MOF-801 with high proton conductivity and its composite membrane for proton-exchange membrane. *ACS applied materials & interfaces* **2018,** *10* (34), 28656-28663.