Sulfonated covalent organic framework packed nafion membrane with high proton conductivity for H_2/O_2 fuel cell applications

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Supporting Information

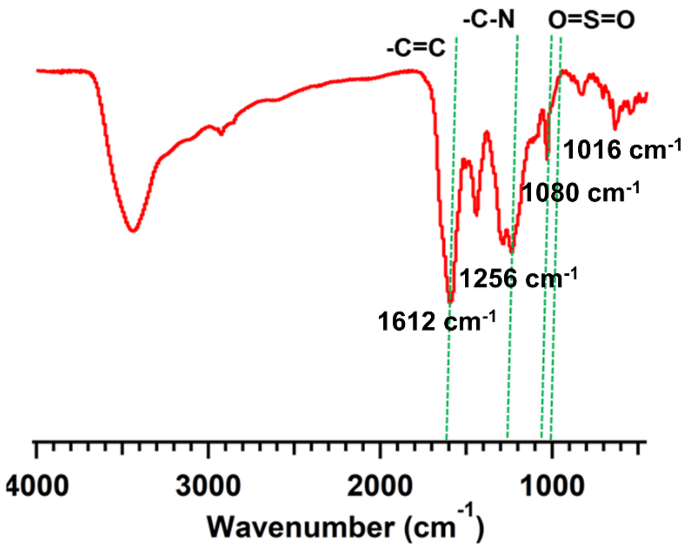

Fig. S1 Infrared spectrum of ZUT-COF-SO_3H.

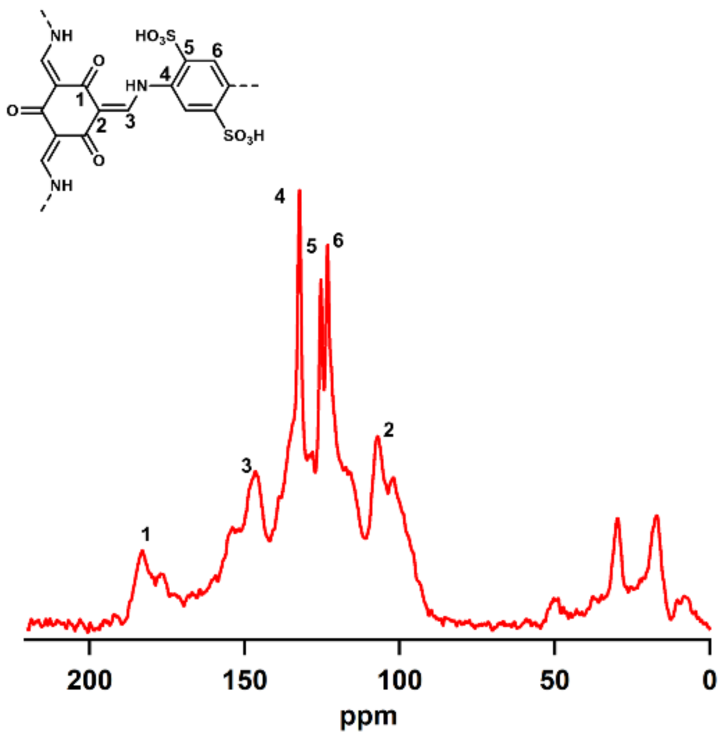

Fig. S2 Solid state ^{13}C NMR of ZUT-COF-SO_3H.

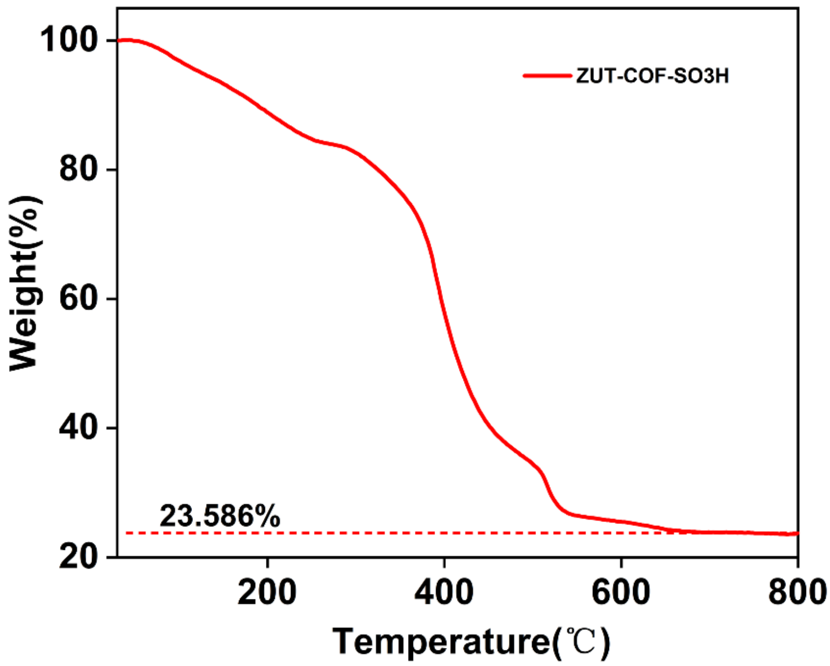

Fig. S3 Thermogravimetric analysis of ZUT-COF-SO_3H.

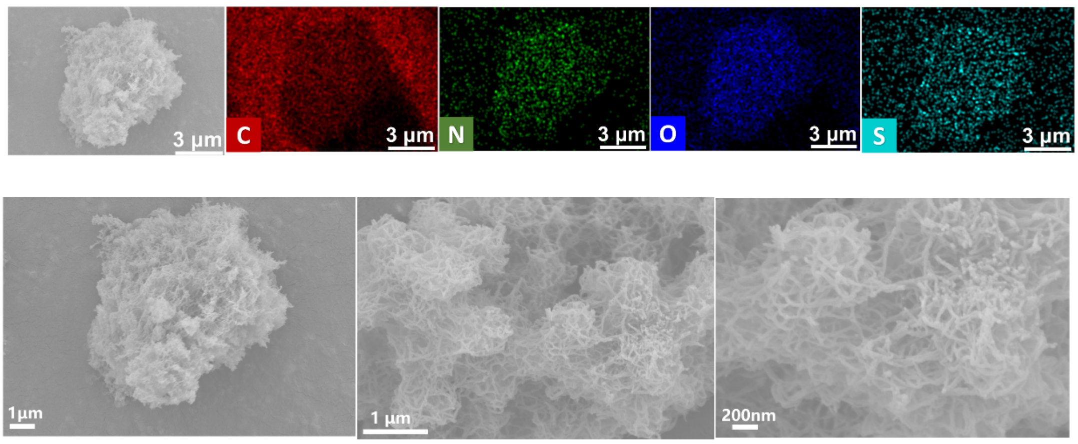

Fig. S4 SEM and mapping images of ZUT-COF-SO_3H.

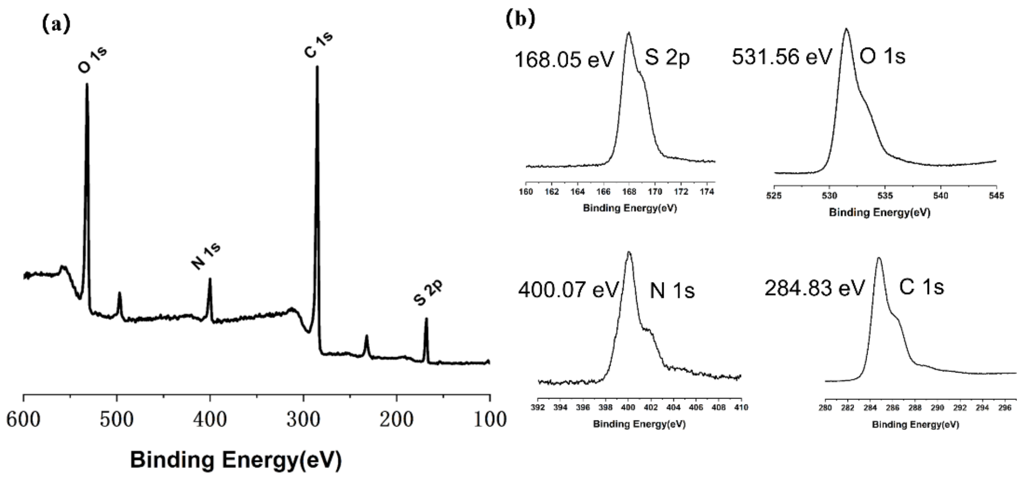

Fig. S5 XPS spectrum of ZUT-COF-SO_3H.

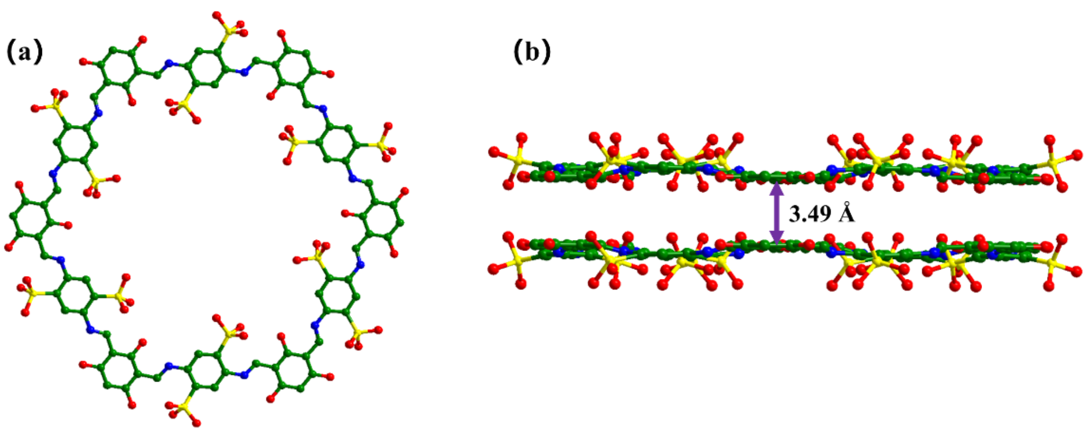

Fig. S6 The distance between different layers in the AA stacking mode.

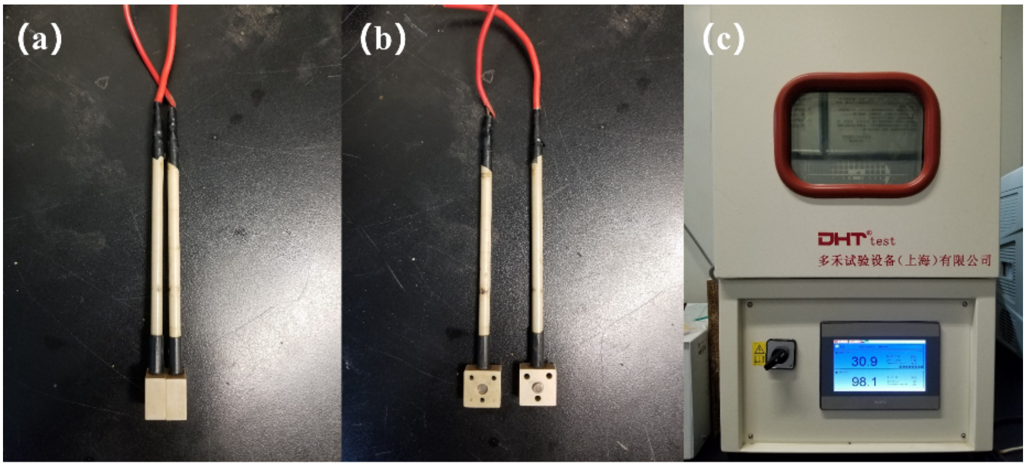

Fig. S7 Sample preparation and test equipment: (a, b) test electrode, (c) constant temperature and humidity oven.

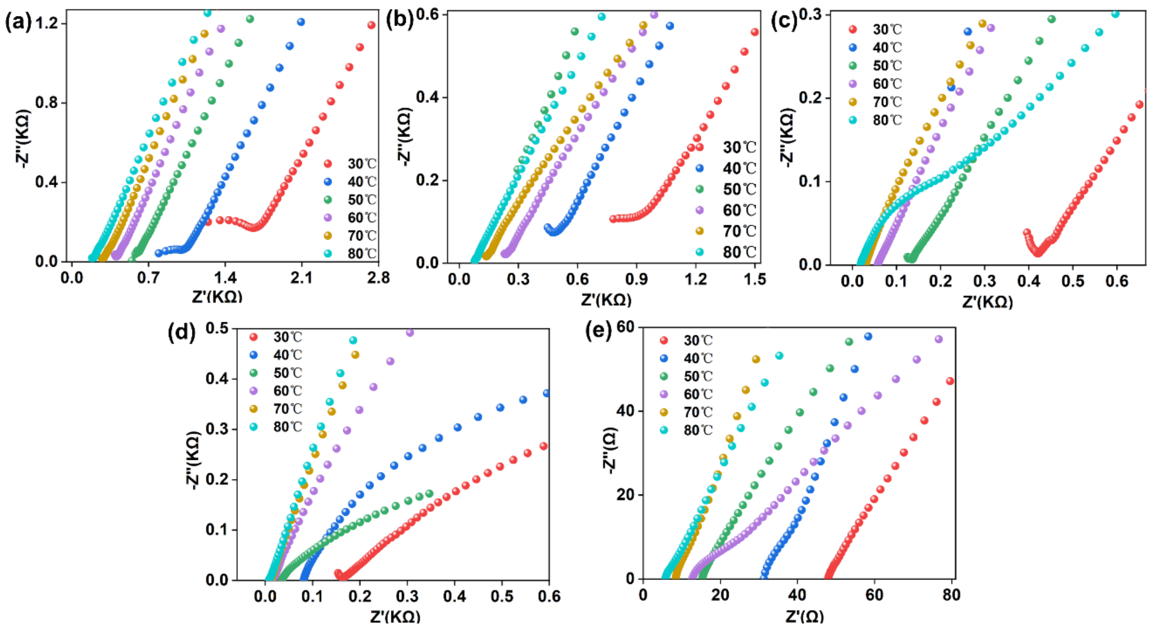

Fig. S8 Impedance spectra of ZUT-COF-SO_3H at different humidity,(a)60%, (b)70%, (c)80%, (d)90%, (e)98%.

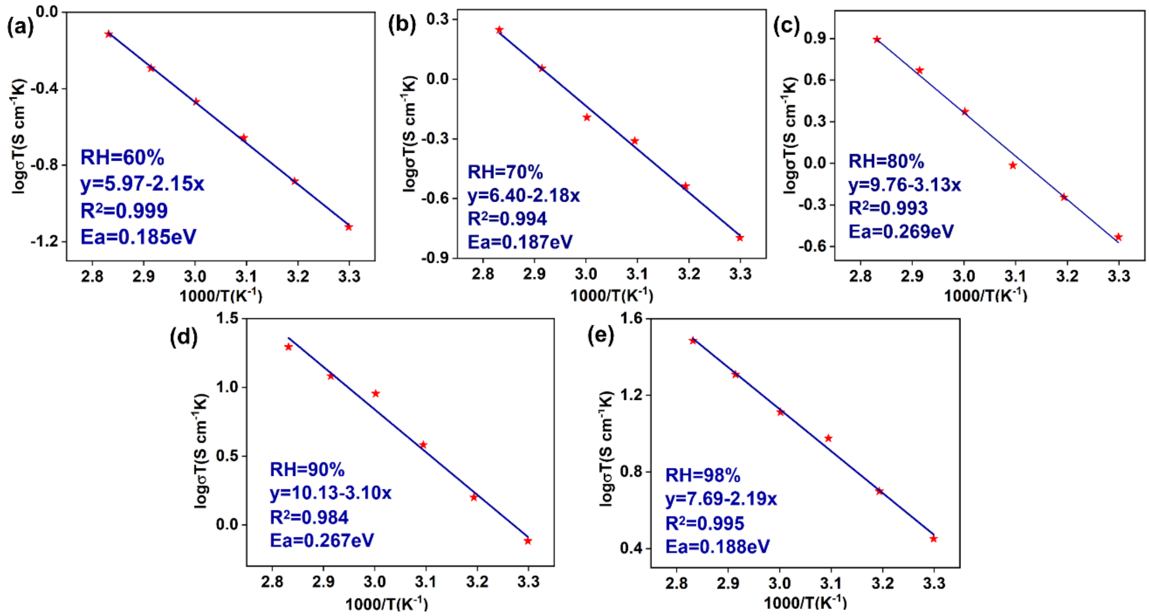

Fig. S9 Activation energy of ZUT-COF-SO_3H at different humidity,(a)60%, (b)70%, (c)80%, (d)90%, (e)98%.

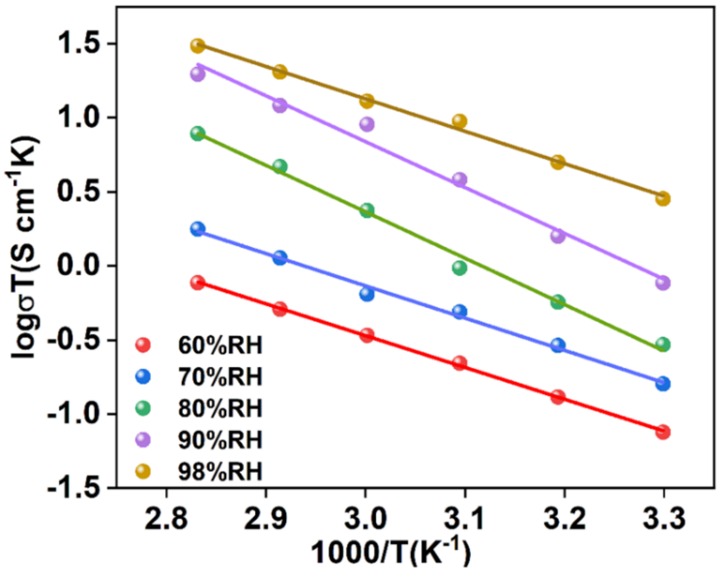

Fig. S10 Arrhenius curve of ZUT-COF-SO_3H at different humidity.

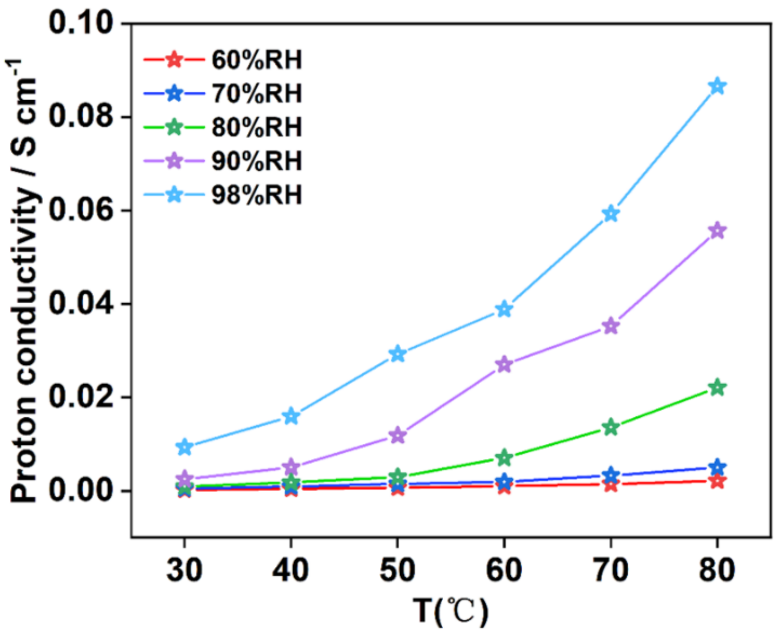

Fig. S11 Temperature-dependent proton conductivity of ZUT-COF-SO_3H.

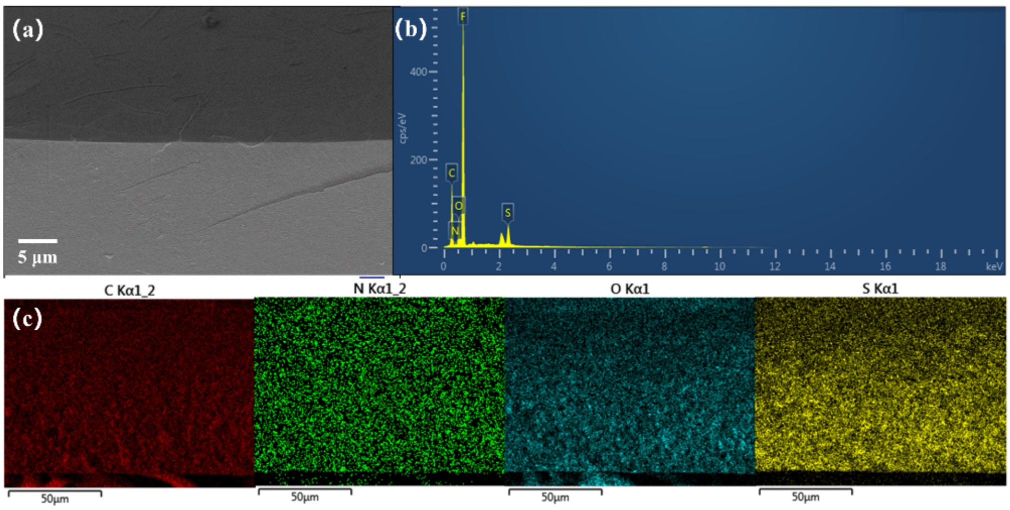

Fig. S12 SEM and EDS of ZUT-COF-SO_3H@Nafion cross section.

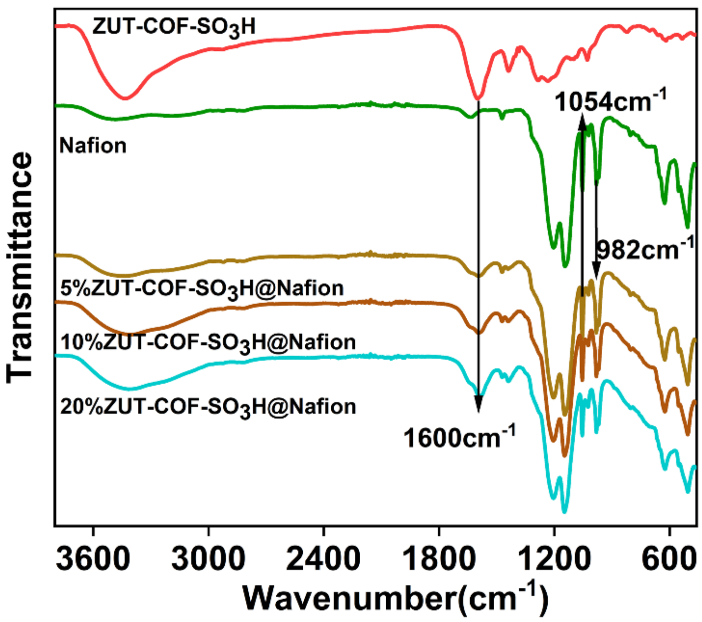

Fig. S13 Infrared spectrum of ZUT-COF-SO_3H@Nafion hybrid membranes.

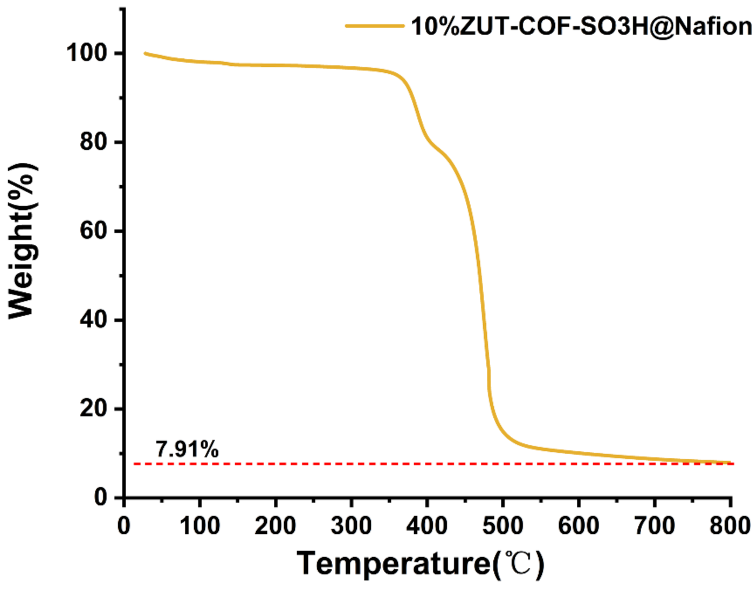

Fig. S14 Thermogravimetric analysis of 10%ZUT-COF-SO_3H@Nafion hybrid membranes

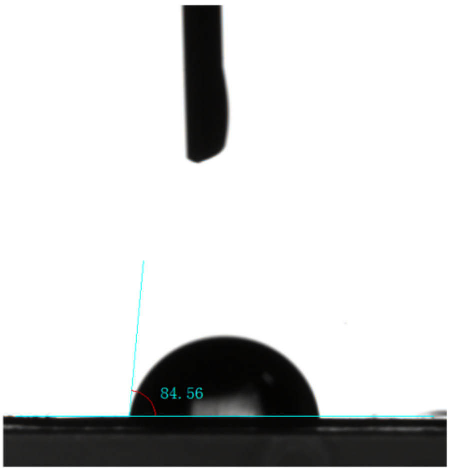

Fig. S15 Water contact angle of 10%-ZUT-COF-SO_3H@Nafion.

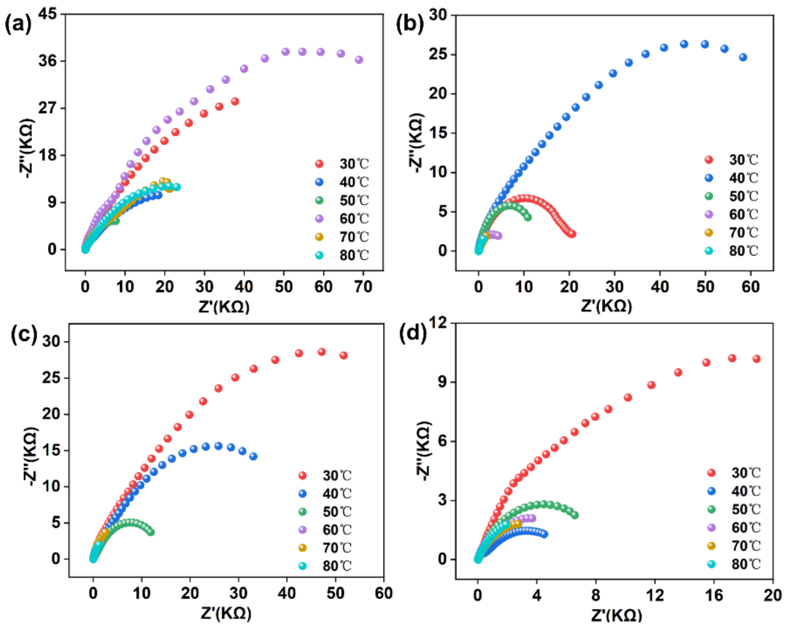

Fig. S16 Impedance spectra of ZUT-COF-SO_3H@Nafion hybrid membranes with different loading at 80%RH, (a)0%, (b) 5%, (b) 10%, (b)20%.

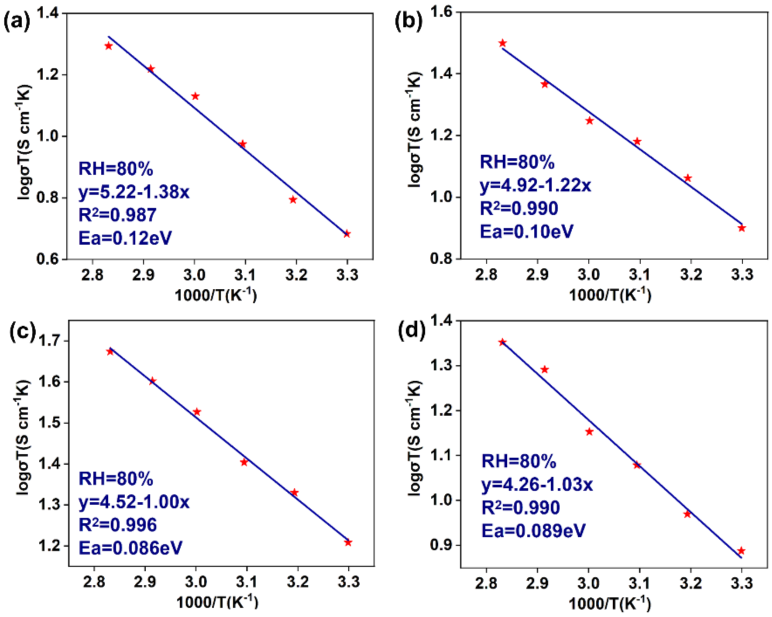

Fig. S17 Activation energy of ZUT-COF-SO_3H@Nafion hybrid membranes with different loading (a)0%, (b) 5%, (b) 10%, (b)20%.

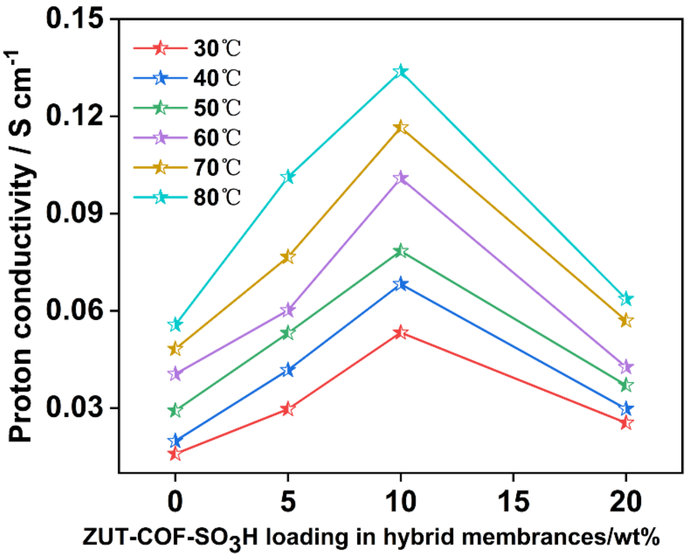

Fig. S18 Proton conductivity of ZUT-COF-SO3H@Nafion hybrid membranes with different loading.

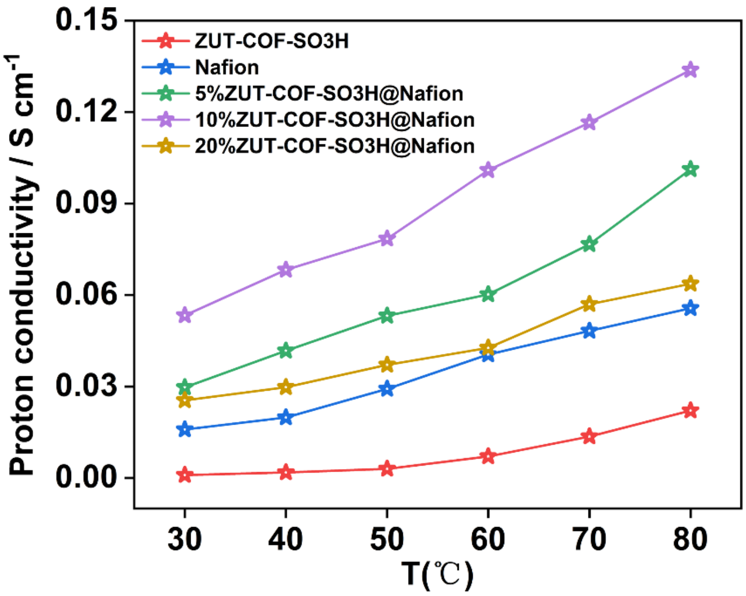

Fig. S19 Temperature-dependent proton conductivity of ZUT-COF-SO$_3$H@Nafion hybrid membranes with different loading.

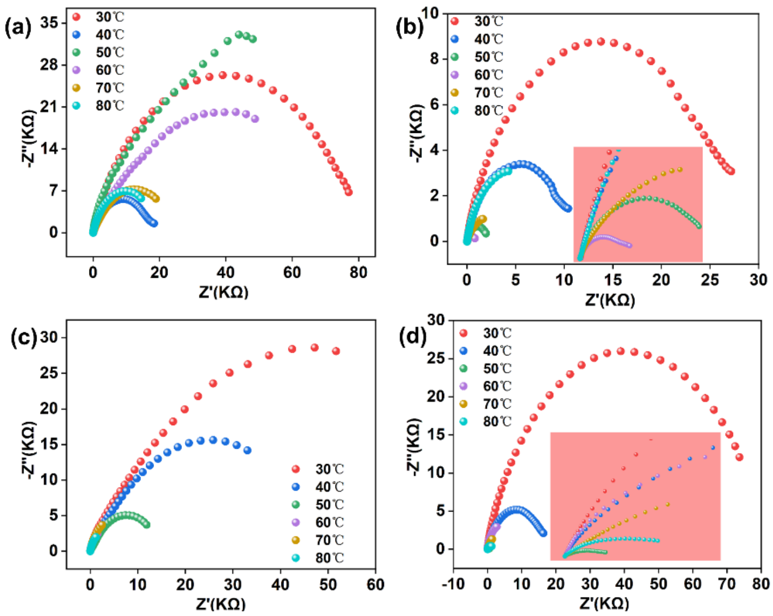

Fig. S20 Impedance spectra of 10%ZUT-COF-SO$_3$H@Nafion hybrid membranes at different humidity, (a)60%, (b)70%, (c)80%, (d)90%.

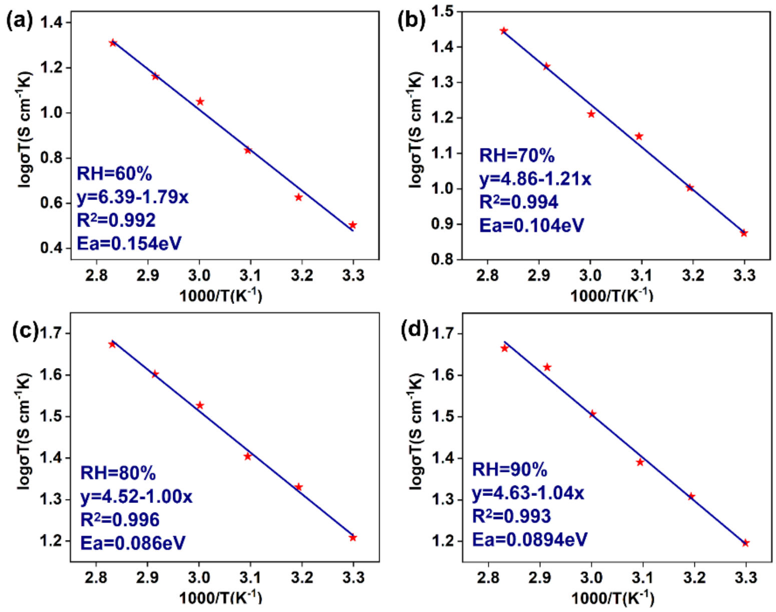

Fig. S21 Activation energy of 10%ZUT-COF-SO_3H@Nafion hybrid membranes at different humidity, (a)60%, (b)70%, (c)80%, (d)90%.

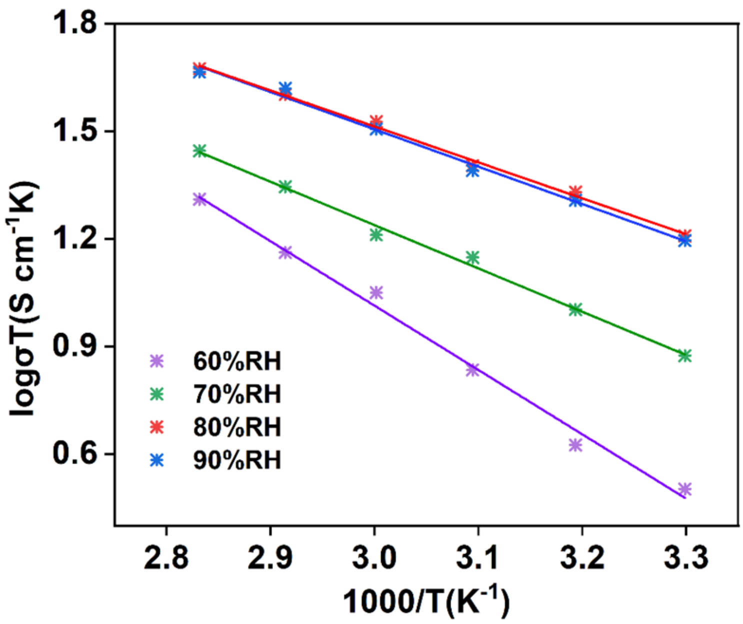

Fig. S22 Arrhenius curve of 10%ZUT-COF-SO_3H@Nafion hybrid membranes at different humidity.

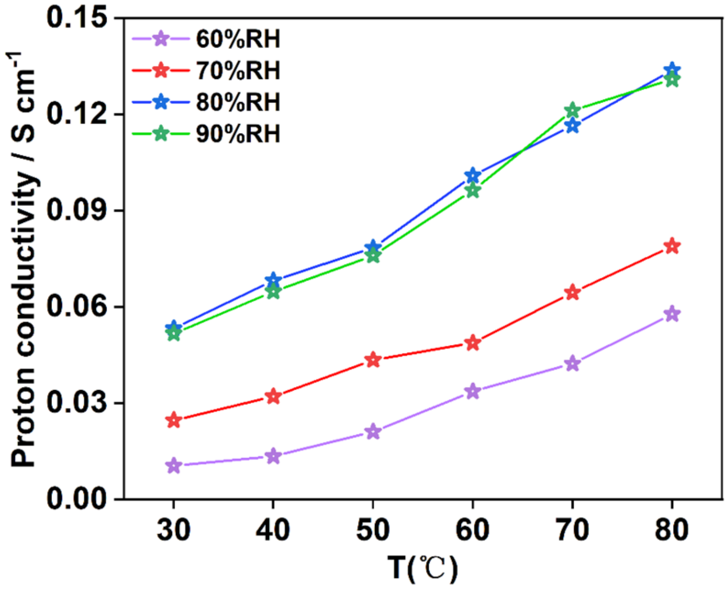

Fig. S23 Proton conductivity of 10%ZUT-COF-SO_3H@Nafion hybrid membranes.

Table S1 Performance comparisons of proton conductivity with other reported material.

Materials	Proton conductivi	Test environment	Reference
MIL-101-SO_3H	1.16×10^{-2}	100%RH, 80 ºC	S1
KAUST-7′	2.2×10^{-2}	95%RH, 90 ºC	S2
$\{[Cu_3L_2(H_2O)_6]\cdot2H_2O\}_n$	4.08×10^{-3}	100%RH, 95 ºC	S3
B-PCMOF-2	1.3×10^{-3}	90%RH, 85 ºC	S4
Mg(p-BDC)(PyOH)_Cs	1.61×10^{-2}	90%RH, 90 ºC	S5
$\{[Fe^{III}{}_3L_2(H_2O)_6]\bullet3(OH)\}_n$/PVP/PVDF-10	1.77×10^{-3}	98%RH, 80 ºC	S6
N_U_{200}-2	1.65×10^{-1}	95%RH, 80 ºC	S7
N_U_{200}-10	7.9×10^{-2}	95%RH, 80 ºC	S7
TpBD-$(SO_3H)_2$ iCOFMs	6.6×10^{-1}	100%RH, 90 ºC	S8
BIY-COF	1.9×10^{-2}	95%RH, 95 ºC	S9
TFPPY-BT-COF-H_2PO_3	1.12×10^{-3}	98%RH, 60 ºC	S10
TFPPY-PDA-COF-H_2PO_3	1.34×10^{-4}	98%RH, 60 ºC	S10
Nafion	~1×10^{-1}	98%RH, 80 ºC	S11
BIP-COF	3.2×10^{-2}	95%RH, 95 ºC	S12
H_3PO_4@NKCOF-1	1.13×10^{-1}	98%RH, 80 ºC	S13
H_3PO_4@NKCOF-2	4.28×10^{-2}	98%RH, 80 ºC	S13
H_3PO_4@NKCOF-3	1.12×10^{-2}	98%RH, 80 ºC	S13
H_3PO_4@NKCOF-4	7.71×10^{-2}	98%RH, 80 ºC	S13
aza-COF-1H	1.23×10^{-3}	97%RH, 50 ºC	S14
aza-COF-2H	4.8×10^{-3}	97%RH, 50 ºC	S14
RT-COF-1Ac	1.07×10^{-4}	100%RH, 40 ºC	S15
PTSA@TpAzoCOFM	7.8×10^{-2}	95%RH, 80 ºC	S16
ZUT-COF-SO_3H	8.65×10^{-2}	98%RH, 80 ºC	This work
10%ZUT-COF-SO_3H@Nafion	1.338×10^{-1}	80%RH, 80 ºC	This work

Table S2 Performance comparisons of power density with other reported materials.

Samples	Power Density mW cm^{-2}	*Ref.*
SPEEK/2#-10	104.5	*Adv. Funct. Mater.* 2012, **22**, 4539–4546
RN–PQD–5%	407	*Adv. Mater.* 2018, **30**, 1707516
SPEEK/HPW@mGO-4	120.1	*Ind. Eng. Chem. Res*. 2021, **60**, 4460−4470
QOPBI-15	260	*J. Membr. Sci.* 2020*,* **593**,117435
OPBI	190	
SPAES/ATP\/P-CNOs-2	752	*J. Membr. Sci.* 2022, **660**, 120774
PANI-30%-OPBI	250	*Journal of Power Sources,* 2022, 528, 231218
10%-ILs/NH_2-CNTs/OPBI	291	*Journal of Power Sources,* 2022, 543, *231802*
ImPOSS-Nafion	246	*RSC Adv.,* 2013, **3**, 5438–5446
M-3#/PA	280	*Ind. Eng. Chem. Res*. 2017, **56**, 10227−10234
10%ZUT-COF-SO_3H@Nafion	**304.056**	**This work**

References

[S1] S. N. Zhao, X. Z. Song, M. Zhu, X. Meng, L. L. Wu, S. Y. Song, C. Wang and H. J. Zhang, *Dalton Trans.,* 2015, **44**, 948–954.

[S2] X. Wang, Y. L. Wang, M. A. Silver, D. X. Gui, Z. L. Bai, Y. X. Wang, W. Liu, L. H. Chen, J. D. Wu, Z. F. Chai and S. A. Wang, *Chem. Commun.,* 2018*,* **54***,* 4429–4432.

[S3] D. A. Levenson, J. F. Zhang, P. M. J. Szell, D. L. Bryce, B. S. Gelfand, R. P. S. Huynh, N. D. Fylstra, and G. K. H. Shimizu, *Chem. Mater.,* 2020, **32***,* 679−687.

[S4] H. F. Wang, Q. Wu, X. Y. Ding, Z. C. Shao, W. J. Xu, Y. J. Zhao, Q. Xie, X. R. Meng, and H. W. Hou, *Inorg. Chem.,* 2020*,* **59***,* 8361−8368.

[S5] S. Kim, B. Joarder, J. A. Hurd, J. Zhang, K. W. Dawson, B. S. Gelfand, N. E. Wong, and G. K. H. Shimizu, *J. Am. Chem. Soc*., 2018, **140**, 1077−108.

[S6] T. Y. Wen, Z. C. Shao, H. F. Wang, Y. J. Zhao, Y. Cui, and H. W. Hou, *Inorg. Chem.,* 2021*,* **60***,* 18889−18898.

[S7] A. Donnadio, R. Narducci, M. Casciola, F. Marmottini, R. D'Amato, M. Jazestani, H. Chiniforoshan, and F. Costantino, *ACS Appl. Mater. Interfaces,* 2017*,* **9***,* 42239−42246.

[S8] X. Y. Wang, B. B. Shi, H. Yang, J. Y. Guan, X. Liang, C. Y. Fan, X. D. You, Y. A. Wang, Z. Zhang, H. Wu, T. Cheng, R. N. Zhang and Z. Y. Jiang, *Nat Commun.,* 2022, **13***,* 1020*.*

[S9] S. Z. Yang, C. Q. Yang, C. C. Dun, H. Y. Mao, R. S. H. Khoo, L. M. Klivansky, J. A. Reimer, J. J. Urban, J. Zhang, and Y. Liu, *J. Am. Chem. Soc.,* 2022*,* **144***,* 9827−9835.

[S10] Z. W. Lu, C. Y. Yang, L. He, J. Hong, C. H. Huang, T. Wu, X. Wang, Z. F. Wu, X. H. Liu, Z. X. Miao, B. R. Zeng, Y. T. Xu, C. H. Yuan, and L. Z. Dai, *J. Am. Chem. Soc.,* 2022*,* **144***,* 9624−9633.

[S11] X. M. Wu, X. W. Wang, G. H. He, J. Benziger, *J. Polym. Sci. B Polym. Phys*., 2011, **49**, 1437−1445.

[S12] K. C. Ranjeesh, R. Illathvalappil, S. D.Veer, J. Peter, V. C. Wakchaure, Goudappagouda, K. V. Raj, S. Kurungot, and S. S. Babu, *J. Am. Chem. Soc.,* 2019*,* **141***,* 14950−14954.

[S13] Y. Yang, X. Y. He, P. H. Zhang, Y. H. Andaloussi, H. Zhang, Z. Y. Jiang, Y. Chen, S. Q. Ma, P. Cheng, and Z. J. Zhang, *Angew. Chem. Int. Ed.,* 2020*,* **59***,* 3678–3684.

[S14] Z. Meng, A. Aykanat, and K. A. Mirica, *Chem. Mater.,* 2019*,* **31***,* 819−825.

[S15] C. Montoro, D. R. S. Miguel, E. Polo, R. E. Cid, M. L. R. Gonzalez, J. A. R. Navarro, P. Ocon, and F. Zamora, *J. Am. Chem. Soc.,* 2017*,* **139***,* 10079−10086.

[S16] H. S. Sasmal, H. B. Aiyappa, S. N. Bhange, S. Karak, A. Halder, S. Kurungot, and R. Banerjee, *Angew. Chem. Int. Ed.,* 2018*,* **57***,* 10894–10898.