

*Electronic Supplementary Information for:*

**Enhanced proton conduction of crystalline organic salt  
hybrid membranes and performance of fuel cells**

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## ***Section S1. Materials and methods***

Benzenediamine and Nafion solution (20 wt%) were obtained from commercial suppliers. H<sub>4</sub>-TPE was synthesized according to public reports<sup>1</sup>. Unless otherwise stated, all starting solvents and materials can be used without further purification.

### ***Synthesis of HCOS-1***

Dissolve 22.5 mg H<sub>4</sub>-TPE completely in 2 mL water and 1 mL N, N'-dimethylformamide, 20.5 mg benzediamine completely dissolved in 0.5 mL methanol and 0.5 mL N, N-dimethylformamide, two the solution was mixed, kept clear, and allowed to stand at room temperature for 3-4 days to obtain yellow transparent crystals. The yield was 74%. IR (cm<sup>-1</sup>, KBr): 3348 (m), 3341(m), 3281 (w) 2897 (w), 2606 (w), 1610 (s), 1550 (m), 1500 (s), 1396 (m), 1211 (s), 1177 (s), 1121 (s), 1034 (s), 1005 (s). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 7.52–7.45 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 6.98–6.89 (m, 2H) ppm.

The crystals of **HCOS-1** were soaked in water for three days, refluxed in boiling water for 24 hours, and then the water-treated solid was filtered out and dried at room temperature for PXRD measurement. The chemical stability test is as follows: Disperse the crystals of the sample in HCl or NaOH aqueous solutions with different pH values for 24 hours (pH = 3, 11). After that, the solid was filtered out and dried at room temperature for PXRD to determine its stability.

### ***Preparation of composite membranes***

**3%-HCOS-1/Nafion** composite membranes: the crystals of **HCOS-1**(9 mg) were dispersed in 2-propanol (3 mL) under stirring for 2 h, Nafion solution (3 g) were added

to the suspension solution, then the mixture was continue stirring at room temperature for 6 h to give a homogeneous solution. This resultant mixture was poured onto a glass slide, which was dried at room temperature for 24 h for removing solutions. The composite membrane was treated with 3 wt% H<sub>2</sub>O<sub>2</sub>, deionized water and 1 M sulfuric acid solution for 1 h at 80 °C, respectively. After that, the membranes were washed with deionized water until the pH of the surface of membranes were neutral and then dried at room temperature to get membranes for testing.

**6%-HCOS-1/Nafion** composite membranes: the crystals of **HCOS-1** (18 mg) were dispersed in 2-propanol (3 mL) under stirring for 2 h, Nafion solution (3 g) were added to the suspension solution, then the mixture was continue stirring at room temperature for 6 h to give a homogeneous solution. This resultant mixture was poured onto a glass slide, which was dried at room temperature for 24 h for removing solutions. The composite membrane was treated with 3 wt% H<sub>2</sub>O<sub>2</sub>, deionized water and 1 M sulfuric acid solution for 1 h at 80 °C, respectively. After that, the membranes were washed with deionized water until the pH of the surface of membranes were neutral and then dried at room temperature to get membranes for testing.

**9%-HCOS-1/Nafion** composite membranes: the crystals of **HCOS-1** (27 mg) were dispersed in 2-propanol (3 mL) under stirring for 2 h, Nafion solution (3 g) were added to the suspension solution, then the mixture was continue stirring at room temperature for 6 h to give a homogeneous solution. This resultant mixture was poured onto a glass slide, which was dried at room temperature for 24 h for removing solutions. The composite membrane was treated with 3 wt% H<sub>2</sub>O<sub>2</sub>, deionized water and 1 M

sulfuric acid solution for 1 h at 80 °C, respectively. After that, the membranes were washed with deionized water until the pH of the surface of membranes were neutral and then dried at room temperature to get membranes for testing.

## ***Section S2: Experimental details.***

### ***Proton Conductivity***

Proton conductivity was evaluated by electrochemical impedance spectroscopy (EIS) using electrochemical work-station (CHI 660E) in a frequency range of 1 Hz to 0.1 MHz with an alternating voltage of 5 mV. The proton conductivity was calculated using the formula, where  $\sigma$  is the proton conductivity in  $\text{S cm}^{-1}$ ,  $L$  is the distance between the two electrodes,  $R$  is the measured resistance, and  $A$  is the area. To evaluate the activation energies, the curves were plotted with logarithms of the product of proton conductivity and temperature ( $\ln(\sigma T)$ ) against the inverse of the temperature ( $1000/T$ ).

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

### ***Instrumentation.***

Powder X-ray diffraction (PXRD) measurements were carried out in Bruker D8 Advance with a Cu X-ray source over a range of  $2\theta = 5.0\sim 55.0^\circ$ . Thermogravimetric analysis (TGA) measurements were performed on a TGA-55 instrument from room temperature to 800 °C at a heating rate of 10 °C/min under air atmosphere. Scanning electron microscope test were performed on a SU8100. The mechanical properties of the membrane are tested on CMT4202 for tensile tester. Fouriertransform infrared (FT-IR) spectra were obtained on a Bruker VECTOR-22 FTIR spectrometer in the 4000~400  $\text{cm}^{-1}$  region with KBr pellets.  $^1\text{H}$  NMR spectra were performed on a Bruker-600 MHz NMR spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal standard.

### ***Stability Experiments***

The crystals of **HCOS-1** were soaked in water for three days and refluxed in boiling water for 24 hours to maintain hydrothermal stability. After water treatment, the crystals were filtered out and dried at room temperature for PXRD measurement. Chemical stability test of **HCOS-1**: Disperse the crystals in HCl or NaOH aqueous solutions of different pH values for 24 hours (pH = 3,12). After that, the solid was filtered and dried at room temperature for PXRD to determine its stability. We also performed a PXRD test on the electrochemical crystal to determine the stability of the electrochemical impedance test.

### ***Area Swelling:***

Cut the composite film into pieces (1×1 cm<sup>2</sup>), and then immerse it in deionized water at room temperature for 24 hours. After that, the sample was taken out of the water, laid flat on a platform, and its size was quickly measured.

$$\Delta S = (S_1 - S_0) / S_0 \times 100\%$$

### ***Water Uptake :***

Intercept a sample of a certain size, weigh its initial mass  $W_0$  with an analytical balance, and then immerse it in deionized water at room temperature for 24 hours. After that, the sample was taken out of the water, the surface was quickly blotted dry with filter paper, and its mass  $W_1$  was quickly weighed.

$$\Delta W = (W_1 - W_0) / W_0 \times 100\%$$

### ***Ion exchange capacity :***

Take a sample with a mass of not less than 0.5 g, cut it into pieces, place it in a 0.1

MPa, 80 °C vacuum drying oven for 8 hours, take it out of the vacuum drying oven and quickly weigh its weight W, put the sample in a sealed, stir in a reagent bottle filled with saturated sodium chloride solution for 24 hours, titrate it with 0.01 mol/L sodium hydroxide solution until it is neutral, and record the volume V of sodium hydroxide solution consumed.

$$IEC = (V_{NaOH} \times C_{NaOH}) / W$$

***Proton exchange membrane performance test.***

The fuel cell performance of composite membrane was evaluated by analyzing the curves of current density versus voltage and power density. The polarization curve is measured by multi-step constant current method. The composite membrane (active area: 5 cm<sup>2</sup>, thickness: 30-40 μm) was sandwiched between the two electrodes and then tested in a fuel cell device at 80 °C under 150 sccm flow rate of H<sub>2</sub> and 600 sccm of air with 0.2 MPa back-pressure and 100% RH gas humidification, the anode catalyst loading was 0.20 mg·cm<sup>-2</sup>, and the cathode was 0.4 mg·cm<sup>-2</sup>.

***Preparation of the MEA.***

The MEA was constructed by inserting the prepared membrane between two electrodes (commercial gas diffusion Pt) then loaded onto a carbon electrode. The MEAs is then thermally pressed into fuel cell hardware in a serpentine flow field with an effective area of 6 square centimeters.



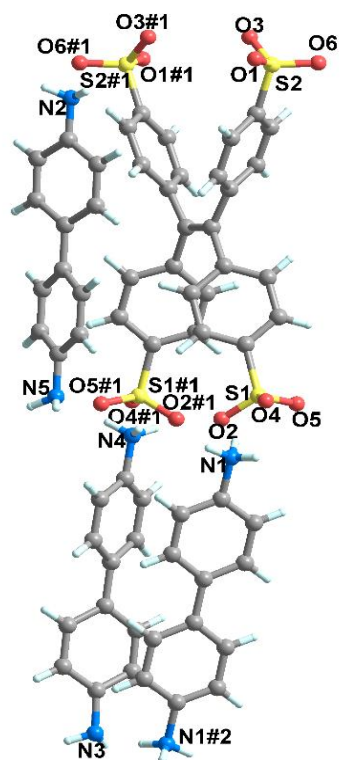
### ***Section S3: Single crystal X-ray diffraction analyses.***

Single-crystal X-ray diffraction data for compound HCOS-1 were collected on a Bruker SMART APEX CCD diffractometer<sup>2</sup> equipped with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$ -scan technique. Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine<sup>3</sup>. All the structures were solved with direct methods (*SHELXS*)<sup>4</sup> and refined by full-matrix least squares on  $F^2$  using *OLEX2*,<sup>5</sup> which utilizes the *SHELXL-2015* module.<sup>6</sup> All non-hydrogen atoms were refined anisotropically. Displacement parameter restraints were used in modeling the ligands. Hydrogen atoms were placed geometrically on their riding atom where possible. The contents of the solvent region are not represented in the unit cell contents in the crystal data. Crystal data containing space group, lattice parameters and other relevant information for the title complex are summarized in Table S1. More details on the crystallographic data are given in the X-ray crystallographic files in CIF format. Full details of the structure determinations have been deposited with Cambridge Crystallographic Data Center under reference number CCDC 2165946 for **HCOS-1**, and is available free of charge from CCDC.

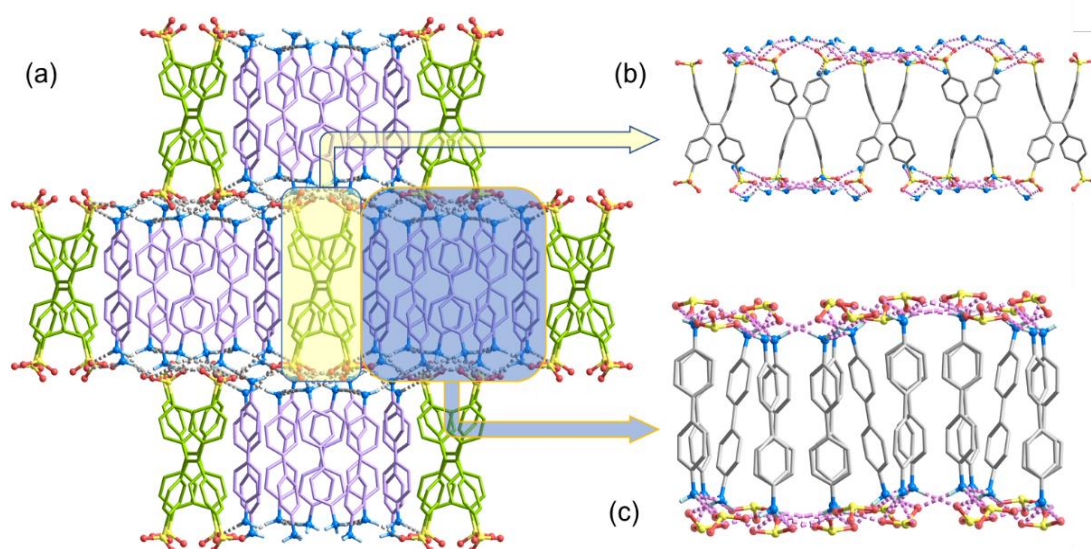
**Table S1.** Crystal structure data and refinement details of **HCOS-1**.

| Compounds  | HCOS-1   |
|--|--|
| Empirical formula  | C <sub>86</sub> H <sub>80</sub> N <sub>10</sub> O <sub>12</sub> S <sub>4</sub> |
| Formula weight   | 1573.84  |
| Temperature / K  | 273.0  |
| Wavelength / Å   | 0.71073  |
| Crystal system   | monoclinic   |
| Space group  | <i>C2/c</i>  |
| <i>a</i> /Å  | 24.255(6)  |
| <i>b</i> /Å  | 24.233(5)  |
| <i>c</i> /Å  | 16.847(4)  |
| <i>α</i> /°  | 90.00  |
| <i>β</i> /°  | 128.006(9)   |
| <i>γ</i> /°  | 90.00  |
| Volume/Å <sup>3</sup>  | 7803(3)  |
| Z  | 4  |
| Density (calculated) / g·cm <sup>-3</sup>  | 1.340  |
| Absorption coefficient / mm <sup>-1</sup>  | 0.192  |
| F(000)   | 3340.0   |
| Reflections collected  | 34422  |
| Independent reflections  | 6856( <i>R</i> <sub>int</sub> = 0.0441, <i>R</i> <sub>sigma</sub> =0.0337)     |
| Data/restraints/parameters   | 6856/0/510   |
| Goodness-of-fit on <i>F</i> <sup>2</sup>   | 1.089  |
| <sup>a</sup> <i>R</i> <sub>1</sub> , <sup>b</sup> <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ ( <i>I</i> )] | 0.0696/0.2035  |
| <sup>a</sup> <i>R</i> <sub>1</sub> , <sup>b</sup> <i>wR</i> <sub>2</sub> (all data)                    | 0.0921/0.2201  |
| Largest diff. peak and hole  | 0.80/-0.58 e·Å <sup>-3</sup>   |
| CCDC number  | 2165946  |

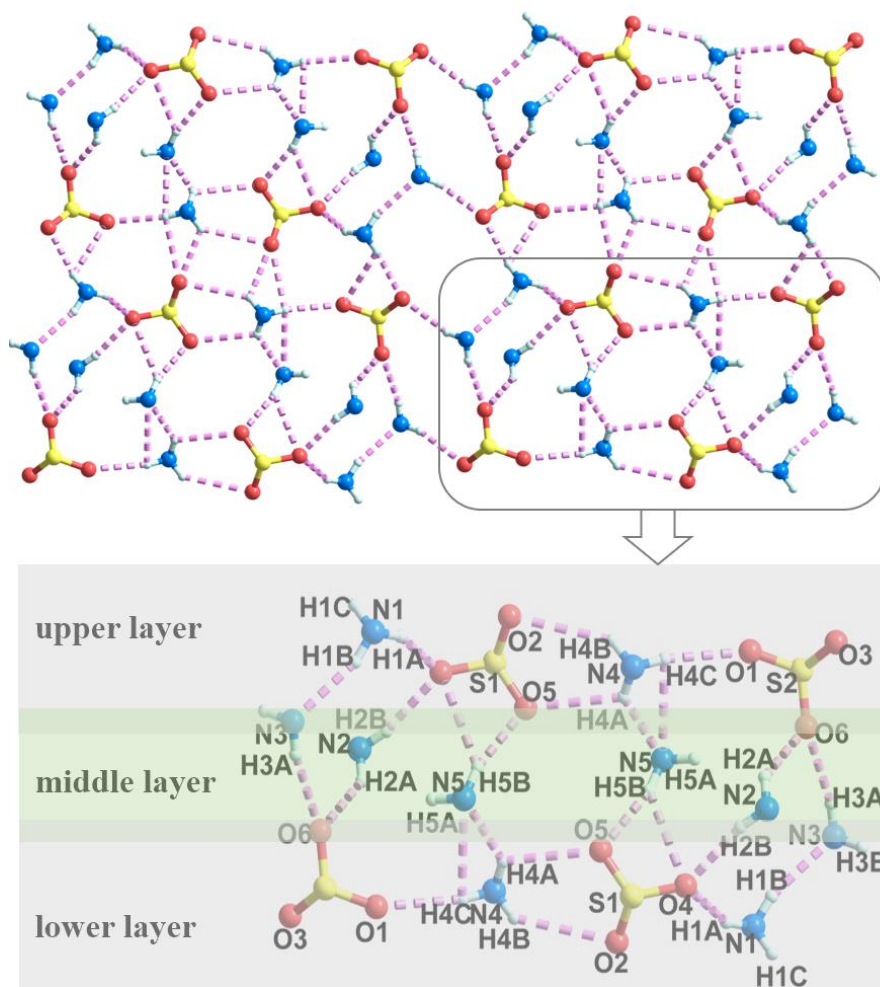
$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$



**Fig. S1.** The asymmetric unit of **HCOS-1**. Symmetry codes: #1:  $1 - x, y, 1/2 - z$ ;  
#2:  $1 - x, -y, 1 - z$ .

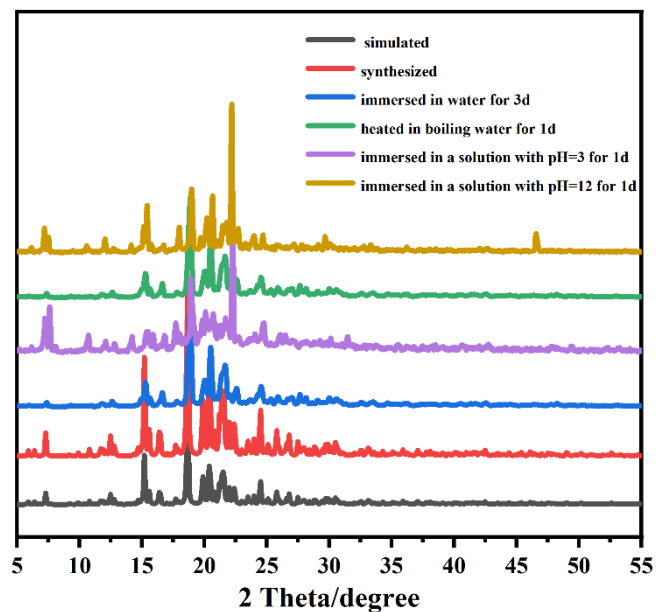


**Fig. S2.** The  $\text{TPE}^{4-}$  and DABP chains connecting with each other through hydrogen bondings in **HCOS-1**.

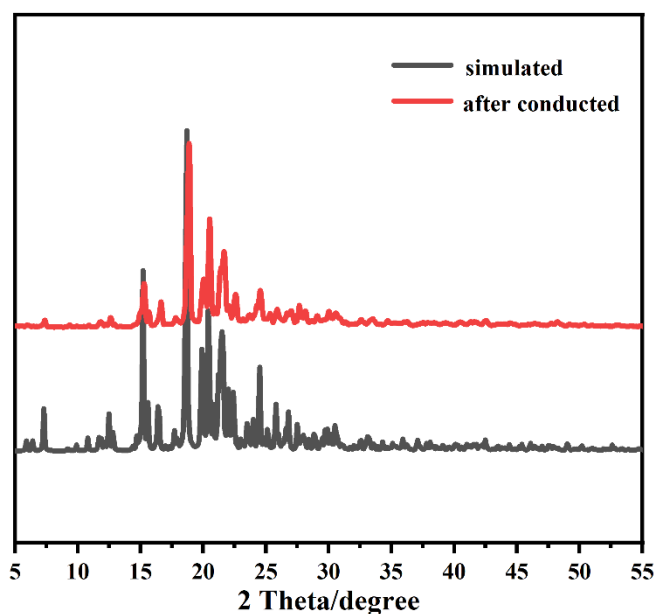


**Fig. S3.** The Partial hydrogen bonding of **HCOS-1**.

*Section S4. PXRD patterns.*

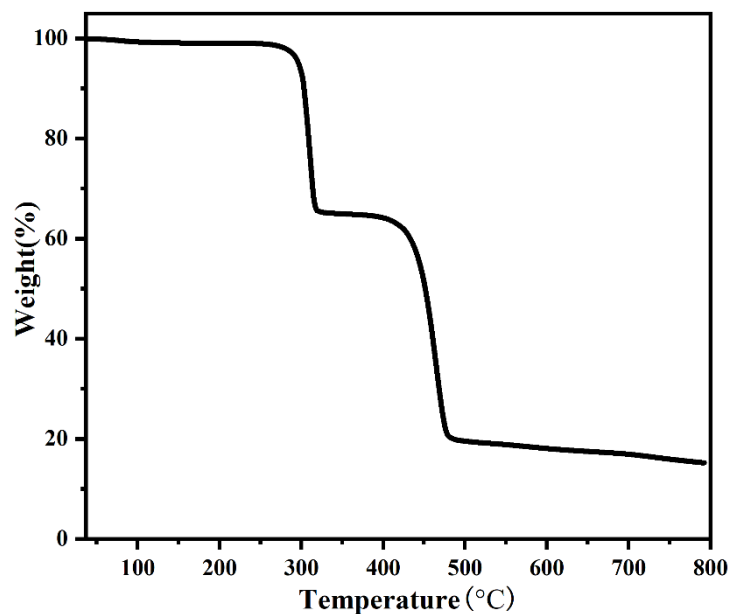


**Fig. S4.** PXRD pattern of **HCOS-1**, immersed in water for three days, heated in boiling water for one day, immersed in a solution with pH = 3 for one day, immersed in a solution with pH = 12 for one day.

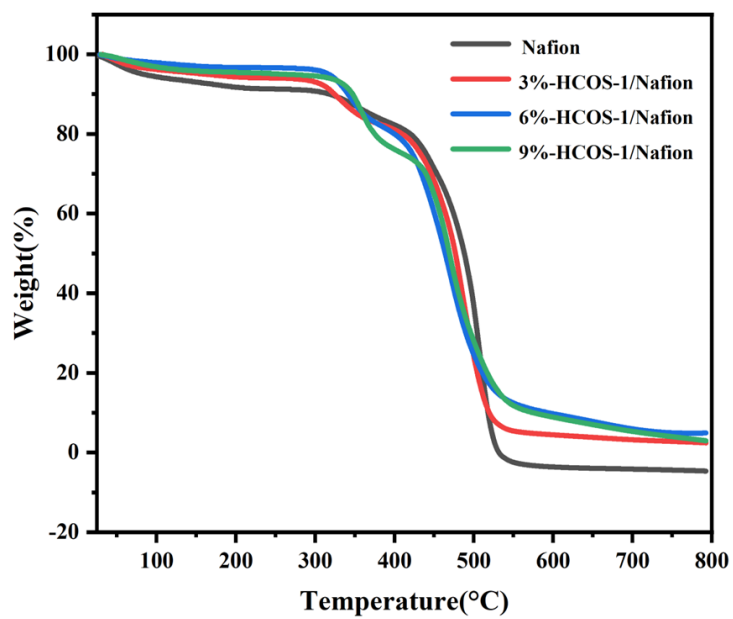


**Fig. S5.** PXRD patterns of **HCOS-1** simulated (black) and after conducted (red).

*Section S5. TG patterns.*

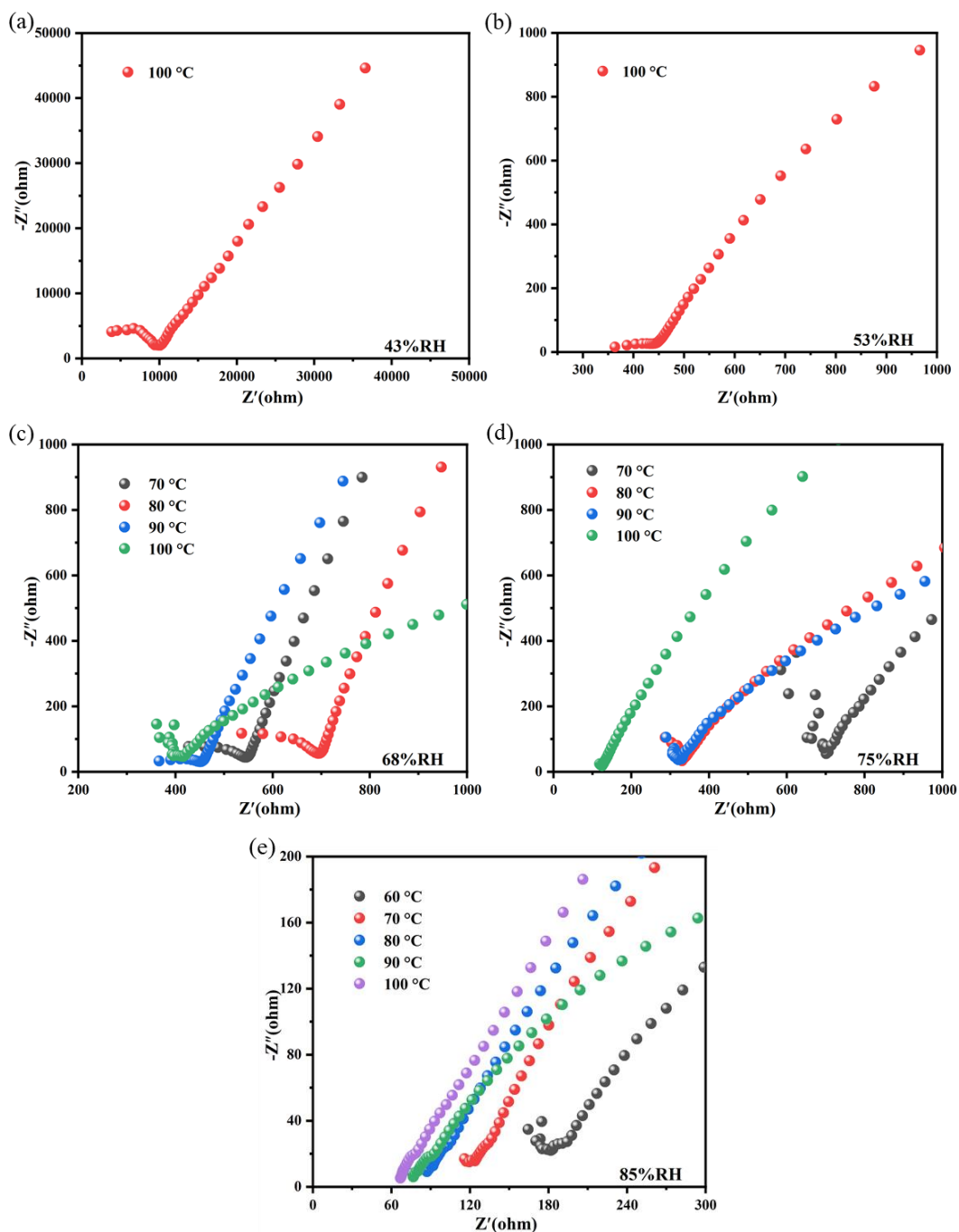


**Fig. S6.**TGA plot of **HCOS-1**.

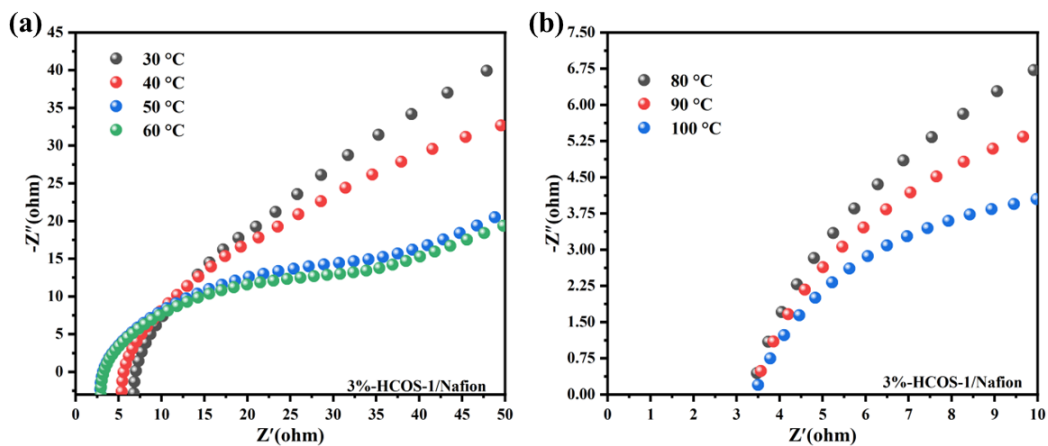


**Fig. S7.**TGA plots of Nafion/HCOS-1 composite membrane

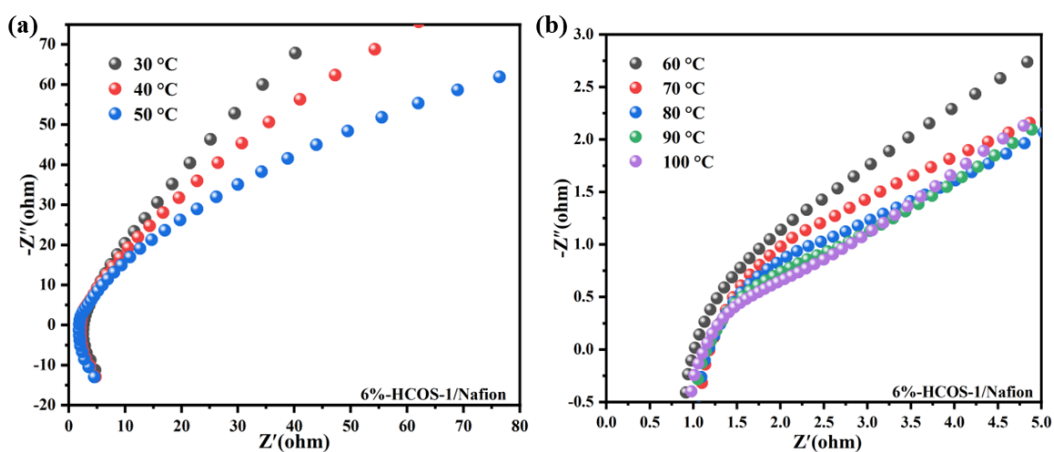
**Section S6. Proton conductivity.**



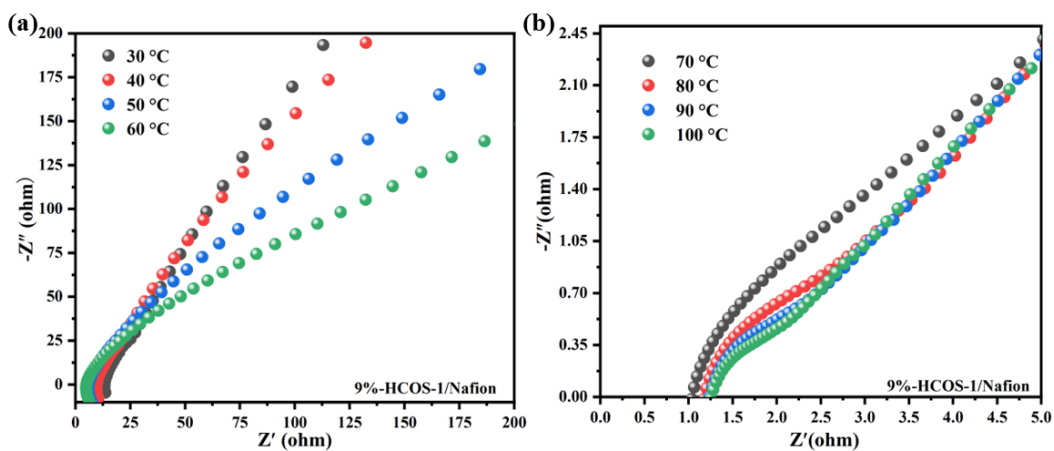
**Fig. S8.** The Nyquist plot of **HCOS-1**: (a) Nyquist plots of **HCOS-1** at 43% RH; (b) Nyquist plots of **HCOS-1** at 53% RH; (c) Nyquist plots of **HCOS-1** at 68% RH; (d) Nyquist plots of **HCOS-1** at 75% RH; (e) Nyquist plots of **HCOS-1** at 93% RH; (e) Nyquist plots of **HCOS-1** at 93% RH



**Fig. S9.** Temperature-dependent proton conductivity of **3%-HCOS-1/Nafion** membranes at 98% RH.

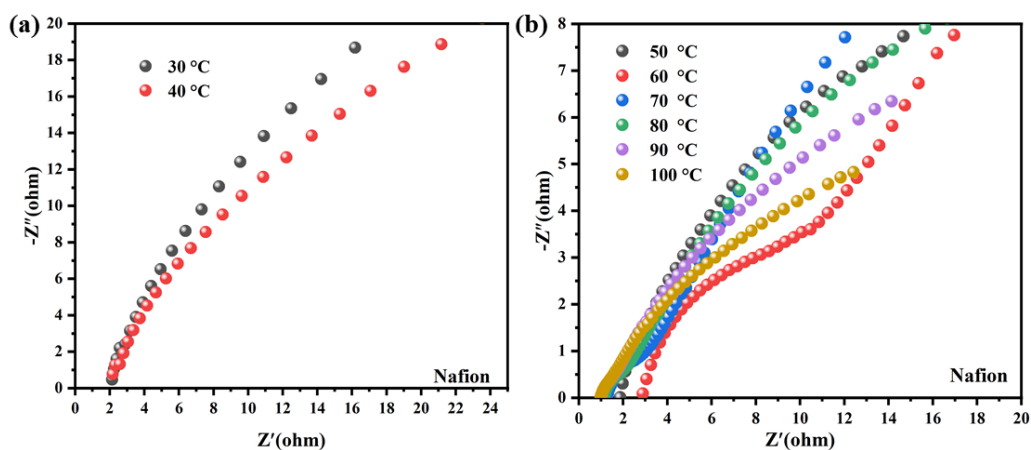


**Fig. S10.** Temperature-dependent proton conductivity of **6%-HCOS-1/Nafion** membranes at 98% RH.

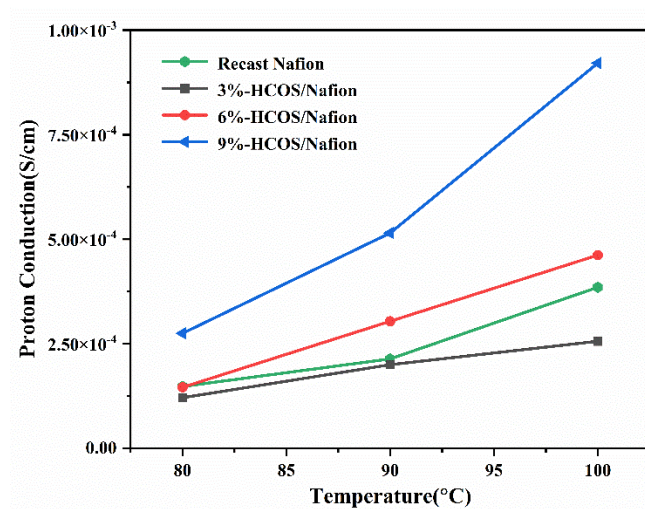


**Fig. S11.** Temperature-dependent proton conductivity of **9%-HCOS-1/Nafion** membranes at 98% RH.





**Fig. S12.** Temperature-dependent proton conductivity of recast **Nafion** membranes at 98% RH.

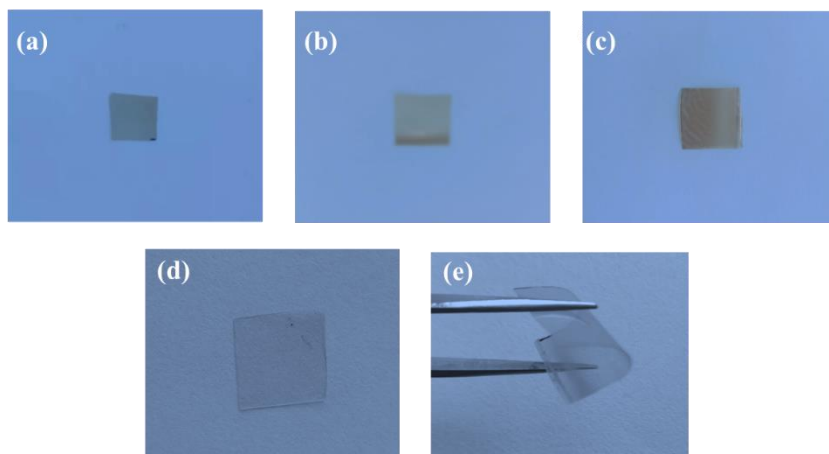


**Fig. S13.** The proton conductivity of the recast **Nafion** and composite membranes at 33% RH.

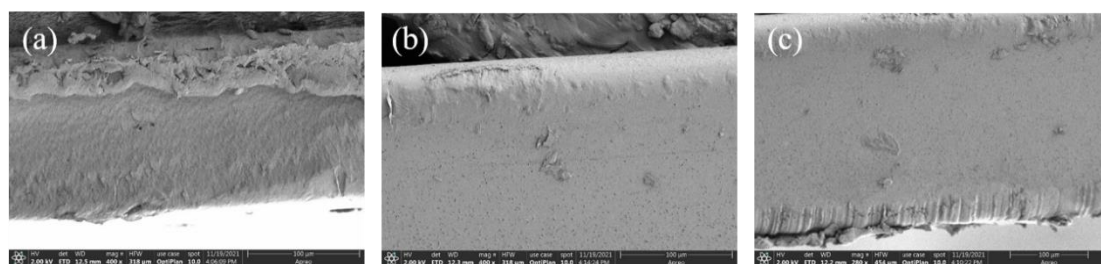
**Table S2.** Proton conductivities ( $\text{S}\cdot\text{cm}^{-1}$ ) for **HCOS-1** at 70~100 °C and different Relative humidity (RH).

|               | 70 °C                 | 80 °C                 | 90 °C                 | 100 °C                |
|---------------|-----------------------|-----------------------|-----------------------|-----------------------|
| <b>68% RH</b> | $1.49 \times 10^{-4}$ | $1.91 \times 10^{-4}$ | $2.27 \times 10^{-4}$ | $2.52 \times 10^{-4}$ |
| <b>75% RH</b> | $1.58 \times 10^{-4}$ | $3.35 \times 10^{-4}$ | $3.45 \times 10^{-4}$ | $8.9 \times 10^{-4}$  |
| <b>85% RH</b> | $8.7 \times 10^{-4}$  | $1.19 \times 10^{-3}$ | $1.35 \times 10^{-3}$ | $1.55 \times 10^{-3}$ |
| <b>93% RH</b> | $1.39 \times 10^{-3}$ | $1.5 \times 10^{-3}$  | $1.68 \times 10^{-3}$ | $3.23 \times 10^{-3}$ |
| <b>98% RH</b> | $8.86 \times 10^{-4}$ | $1.35 \times 10^{-3}$ | $1.58 \times 10^{-3}$ | $1.62 \times 10^{-3}$ |

*Section S7. Scanning electron microscopy and digital imaging*

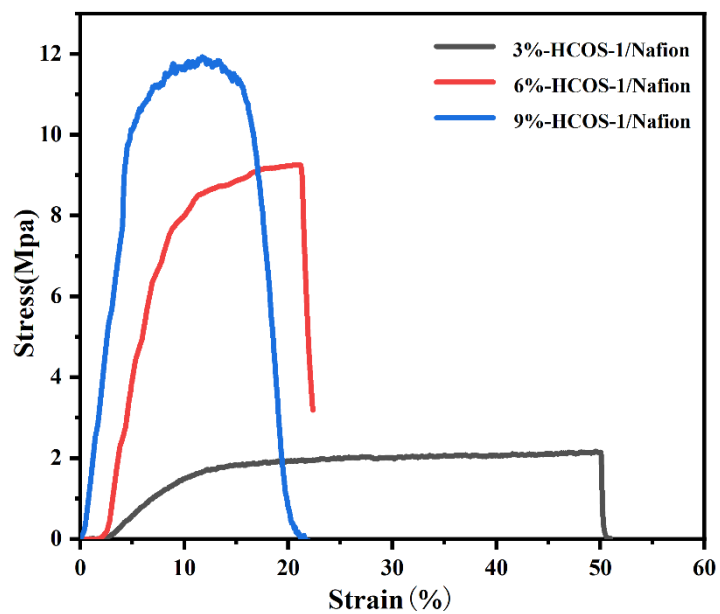


**Fig. S14.** Digital image of the membrane. (a) **3%-HCOS-1/Nafion** composite membrane; (b) **6%-HCOS-1/Nafion** composite membrane; (c) **9%-HCOS-1/Nafion** composite membrane; (d) recast Nafion membrane; (e) **3%-HCOS-1/Nafion** composite membrane bending.



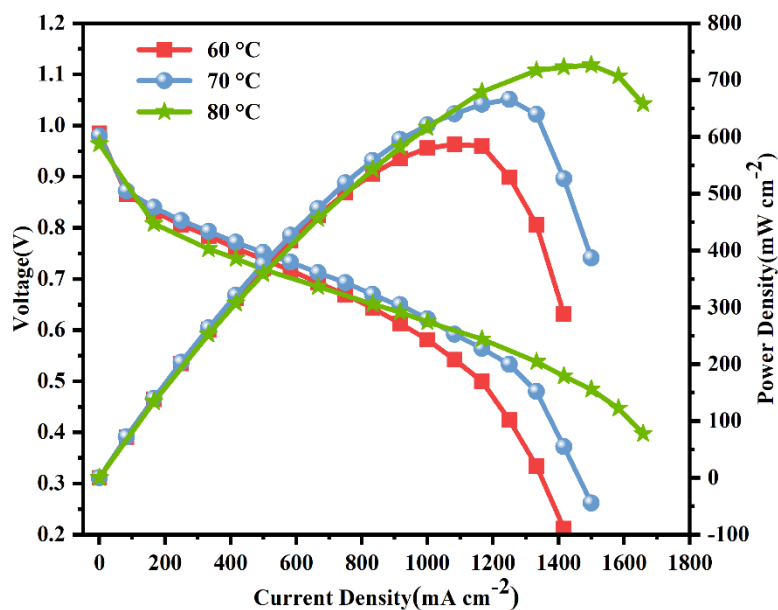
**Fig. S15.** SEM images of the morphology of membrane. (a) The cross sections of **3%-HCOS-1/Nafion** composite membranes; (b) The cross sections of **6%-HCOS-1/Nafion** composite membranes;(c) The cross sections of **9%-HCOS-1/Nafion** composite membranes.

*Section S8. Stress-strain curves.*

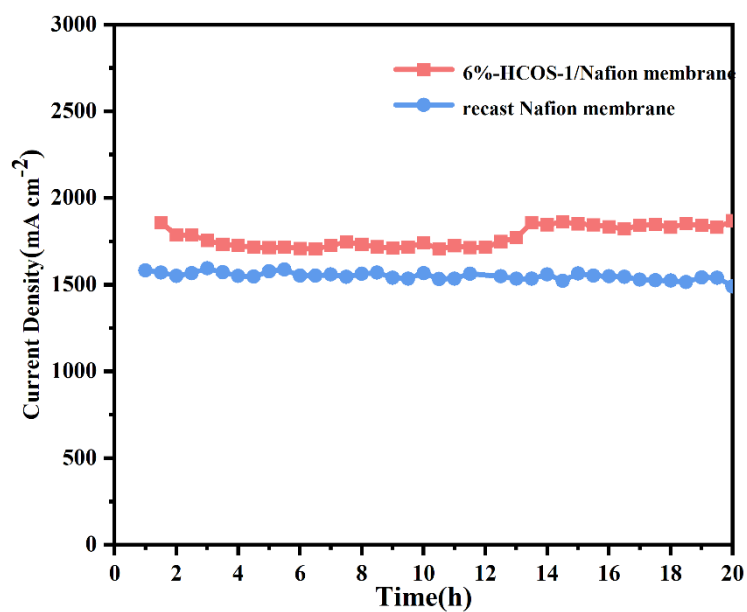


**Fig. S16.** Stress-strain curves of the membranes at room temperature.

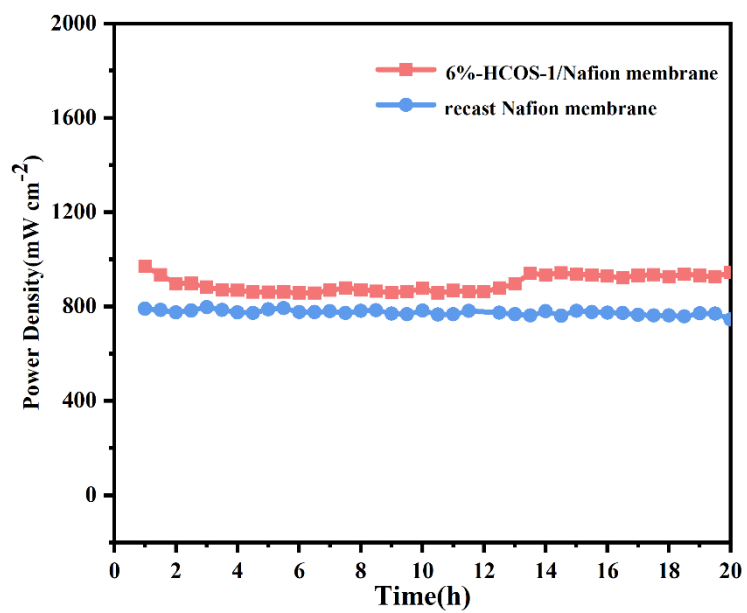
### Section S9. PEMFC performance



**Fig. S17.** Power density and current density of PEMFC ( $\text{H}_2/\text{O}_2$ ) with recast Nafion composite membrane.



**Fig. S18.** Stability comparison of **6%-HCOS-1/Nafion** composite film and recast Nafion film at 20 h current density.



**Fig. S19.** Stability comparison of **6%-HCOS-1/Nafion** composite film and recast Nafion film at 20 h power density.

*Section S10. Ion exchange capacity*

**Table S3.** Ion exchange capacity of composite membrane

| <b>Membranes</b>        | <b>Ion exchange capacity</b> |
|-------------------------|------------------------------|
| <b>Recast Nafion</b>    | <b>0.675 mmol/g</b>          |
| <b>3%-HCOS-1/Nafion</b> | <b>0.728 mmol/g</b>          |
| <b>6%-HCOS-1/Nafion</b> | <b>0.844 mmol/g</b>          |
| <b>9%-HCOS-1/Nafion</b> | <b>1.074 mmol/g</b>          |

## Section S11. Power density of different Nafion hybrid membranes

**Table S4.** Single-Cell Performances of Different Kind of Membrane

| Samples                        | Type of fuel cell              | T(°C) | PD <sub>max</sub><br>(mW/cm <sup>-2</sup> ) | Reference |
|--------------------------------|--------------------------------|-------|---|-----------|
| Nafion/CuTSPc-4.5%             | H <sub>2</sub> /O <sub>2</sub> | RT    | 43.3  | 7         |
| Zn-MOF-NH <sub>3</sub> /Nafion | H <sub>2</sub> /O <sub>2</sub> | 60    | 212   | 8         |
| Nafion/BP <sub>1</sub> -1.0    | H <sub>2</sub> /O <sub>2</sub> | 60    | 276.68                                      | 9         |
| Nafion/BP <sub>4</sub> -1.0    | H <sub>2</sub> /O <sub>2</sub> | 60    | 329.60                                      | 9         |
| Nafion N-115                   | H <sub>2</sub> /O <sub>2</sub> | 70    | 339.57                                      | 9         |
| Nafion/BP <sub>3</sub> -1.0    | H <sub>2</sub> /O <sub>2</sub> | 60    | 343.44                                      | 9         |
| 6%-iHOF-3/Nafion               | H <sub>2</sub> /O <sub>2</sub> | 80    | 360   | 10        |
| Nafion/BP <sub>2</sub> -1.0    | H <sub>2</sub> /O <sub>2</sub> | 70    | 383   | 9         |
| 6%-iHOF-4/Nafion               | H <sub>2</sub> /O <sub>2</sub> | 80    | 420   | 10        |
| Nafion XL                      | H <sub>2</sub> /O <sub>2</sub> | 80    | 961   | 11        |
| 6%-HCOS-1/Nafion               | H <sub>2</sub> /O <sub>2</sub> | 80    | 896   | This work |
| 9%-HCOS-1/Nafion               | H <sub>2</sub> /O <sub>2</sub> | 80    | 734   | This work |



## Section S12. Reference

- [1] Ooyama, Y.; Sugino, M.; EnoKi, T.; Yamamoto, K.; Tsunoji, N.; Ohshita, J., Aggregation-Induced Emission (AIE) Characteristic of Water-Soluble Tetraphenylethene (TPE) Bearing Four Sulfonate Salts. *New J. Chem.* **2017**, *41*, 4747–4749.
- [2] *Smart and Saint. Area Detector Control and Integration Software*; Siemens Analytical X-Ray Systems, Inc.: Madison, W. I. USA, **1996**.
- [3] Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.
- [4] Sheldrick, G. M. *Acta Cryst. A*, **2008**, *64*, 112.
- [5] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339.
- [6] Sheldrick, G. M. *Acta Cryst. C*, **2015**, *71*, 3.
- [7] Wei, Y.; Qian, T.; Liu, J.; Guo, X.; Gong, Q.; Liu, Z.; Tian, B.; Qiao, J. Novel Composite Nafion Membranes Modified with Copper Phthalocyanine Tetrasulfonic Acid Tetrasodium Salt for Fuel Cell Application. *J. Materiomics* **2019**, *5*, 252–257.
- [8] Wang, H.; Zhao, Y.; Shao, Z.; Xu, W.; Wu, Q.; Ding, X.; Hou, H. Proton Conduction of Nafion Hybrid Membranes Promoted by NH<sub>3</sub>-Modified Zn-MOF with Host-Guest Collaborative Hydrogen Bonds for H<sub>2</sub>/O<sub>2</sub> Fuel Cell Applications. *ACS Appl. Mater. Interfaces* **2021**, *13*, 7485–7497.
- [9] Teixeira, F. C.; de Sá, A. I.; Teixeira, A. P. S.; Ortiz-Martínez, V. M.; Ortiz, A.; Ortiz, I.; Rangel, C. M. New Modified Nafion-Bisphosphonic Acid Composite Membranes for Enhanced Proton Conductivity and PEMFC Performance. *Int. J. Hydrog. Energy* **2021**, *46*, 17562–17571.
- [10] Xu, X.-Q.; Cao, L.-H.; Yang, Y.; Zhao, F.; Bai, X.-T.; Zang, S. Q. Hybrid Nafion Membranes of Ionic Hydrogen-Bonded Organic Framework Materials for Proton Conduction and PEMFC Applications. *ACS Appl. Mater. Interfaces* **2021**, *13*, 56566–56574.
- [11] Z. Shang, M. M. Hossain, R. Wycisk and P. N. Pintauro, Poly(phenylene sulfonic acid)-expanded polytetrafluoroethylene composite membrane for low relative humidity operation in hydrogen fuel cells, *J. Power Sources*, **2022**, *535*, 231375.