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## **Supporting information for**

Achieving excellent proton conductivity and power density by introducing stable nitrogen-rich carbonized metal-organic frameworks into high-temperature proton exchange membranes

Jinzhen Huang<sup>1,2</sup>, Gongyi Wei<sup>1</sup>, Jingjing Lin<sup>1</sup>, Jinwu Peng<sup>1,\*</sup>, Lei Wang<sup>1,2,\*</sup>, Jing Liu<sup>1</sup>, Xiaojun Peng<sup>1,2</sup>

<sup>1</sup>Guangdong Provincial Key Laboratory of New Energy Materials Service Safety, Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, China. <sup>2</sup>Zhangjiang Laboratory, 100 Haike Road, Pudong, Shanghai 201210, China.

Corresponding author: Lei Wang, E-mail: wl@szu.edu.cn Jinwu Peng, E-mail: pengjw@szu.edu.cn

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## 1. Characterization method

The chemical structure was confirmed by <sup>1</sup>H NMR spectroscopy recorded on Avance III 500 (Bruker, Germany) and Avance III 600 (Bruker, Germany) with a frequency of 500 MHz and 600 MHz using dimethyl sulfoxide-D<sub>6</sub> (DMSO-d<sub>6</sub>) as the solvent. Morphology of the CU@OPBI and CUN@OPBI membranes was evaluated by using a high-resolution thermal field emission scanning electron microscope (SU-70). The cross-section micrographs were obtained from membranes fractured in liquid nitrogen. Mechanical properties were evaluated by employing a universal testing machine (SANS-CMT4204). The test was processing at a testing speed of 2 mm min<sup>-1</sup> with 4 mm × 17 mm dumbbell samples.

Inherent viscosity determined from a 0.5 g dL<sup>-1</sup> polymer solution in  $H_2SO_4$  (98 %) at 30 °C using Ubbelohde viscometer. All viscosity tests are finished with the same Ubbelohde viscometer.

Oxidative ability of the membrane was investigated by Fenton's test. The 1 cm  $\times$  4 cm rectangular membrane samples were weighed, and then soaked in Fenton reagent (3 wt% H<sub>2</sub>O<sub>2</sub>, 4 ppm Fe<sup>2+</sup>) at 80 °C for 1 day. Took out the samples, repeatedly washed it with distilled water for 3 times. Dried and weighed the samples, measuring the quality curve of the membranes with time.

By measuring the changes of the mass and volume of the membrane with time, the Acid doping level and swelling ratio of the membrane were obtained. Typically, 1  $cm \times 4 cm$  rectangular membrane samples were soaked in 85 wt.% phosphoric acid at 160 °C for 24 h, then took it out, and wiped off the excess phosphoric acid. the samples were dried in a 120 °C oven for 5 h, and the sample weight and size was recorded.

Acid doping level (%) = 
$$\frac{w_2 - w_1}{w_1} \times 100\%$$

Swelling ratio (%) = 
$$\frac{V_2 - V_1}{V_1} \times 100\%$$

where  $w_1$  and  $V_1$  represent the mass and volume of the dry membrane,  $w_2$  and  $V_2$  represent the mass and volume of the PA doped membrane, respectively.

PA retention property could be obtained by fuel cell environmental simulation. PA doped membranes were doped and treated in oven at 80 °C/40% RH. Took out the samples and dried, recording the samples weight for every 24 h.

Proton conductivity was measured by an electrochemical workstation (Zahner IM6ex, Germany) using AC impedance mode with a frequency range of  $1-10^4$  Hz. The PA doped membrane sample (1 cm × 4 cm) was placed into an airtight mold with pure Au electrode. At beginning, the sample was heated at 120 °C for 1.5 h to achieve anhydrous conduction. Then, test the proton conductivity. The temperature range was from 120 °C to 180 °C, and it was balanced for 15 min every 10 °C increase. The proton conductivity ( $\sigma$ ) was calculated according to follow equation:

$$\sigma = \frac{L}{R \cdot S}$$

where L, R and S represent the distance between the pure Au electrodes, the resistance and cross-sectional area of the samples, respectively. The activation energy  $(E_a)$  corresponding to the proton conductivity of membrane materials can be calculated by Arrhenius formula.

$$\sigma = \frac{A}{T} \times e^{\frac{-E_a}{RT}}$$

Fuel cell performance was appraised by single-cell test at 160 °C under anhydrous condition. The membrane-electrode assemblies (MEAs) were prepared by pressing anode and cathode (2.25 cm × 2.25 cm carbon paper electrodes, 1 mg cm<sup>-2</sup> Pt loading, 40 wt.% Pt/C, and 15 wt.% PTFE, Hesen company) onto both sides of proton exchange membranes. Setting gas feeding rates for hydrogen and oxygen were 80 and 160 Sccm, using a multiple independent channel test station (Arbin® MITS PRO 7.0) to record the experiment data.

SmartLab (Rigaku company, Japan) was used for X-ray diffraction (XRD) testing. The testing voltage and current are 40 kV and 200 mA, respectively. The X-ray used is Cu ka ( $\lambda$ ) = 1.5418). The range of 2 $\theta$  is 5-90° (step size is 0.02°). Morphology of the MOFs before and after PA treatment were observed via Field transmission electron microscope (JEM-F200).

The specific surface area and pore size distribution of MOFs and their carbonized derivatives were characterized through nitrogen adsorption and desorption tests. before the tests, the degassing treatment was at 120 °C for 6 h.

The element analyzer (vario EL cube) was used to determine the element content of carbonized MOFs. Before the test, the MOFs were cleaned for three times using N, N-dimethylformamide (DMF), acetone and water respectively, and finally dry under vacuum at 120 °C for 24 h to remove impurities.

2. Characterization results



Fig. S1. TEM morphology of (a) CU, (b) CU-A (CU after a treatment at 120 °C for 24 h), (c) CUN, (d) CUN-A (CUN after a treatment at 120 °C for 24 h).



Fig. S2. Contact Angle test. (a) carbon black, (b) CN and (c) CUN.



Fig. S3. PA uptake-proton conductivity at 160 °C of the PA-doped membranes



Fig. S4 The hydrogen penetration test of the CUN15@OPBI membrane



Fig. S5 the breakdown voltage test of composite membrane



Fig. S6. PA retention ability of OPBI and composite membranes.



Fig. S7. Long-term test of CUN15@OPBI membrane.



Fig. S8 The conductivity of the CUN15@OPBI membrane for 10 h

<b>Table S1</b> Power densities for some reported PBI/x composite membrane
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	Power densities (mW cm <sup>-2</sup> )	s Temperature (°C)	Pt loading (mg cm <sup>-2</sup> )	Ref.
OPBI	523	160	1.0	This work

CU15@OPBI	685	160	1.0	This work
CUN15@OPBI	792	160	1.0	This work
UIO-66@OPBI	546	160	1.0	1
UIO-66-NH <sub>2</sub> @OPBI	728	160	1.0	1
PBI/sGO	364	160	1.0	2
PBI/GO	378	165	1.0	3
PBI-SGO	100	150	0.7	4
PBI-MWNTs	173.5	180	0.25	5
CBOPBI-P40	699	160	1.0	6
50 wt.% HIHBN-PBT- SnPA	750	220	1.0	7
CNTs-NT- <u>TiO2</u> :Nafion <sup>a</sup>	945	80	0.4	8

<sup>a</sup>oxygen, pressurized at 1 bar

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