Supporting information

Two-Dimensional Zeolitic Imidazolate Framework/Carbon Nanotube Hybrid Networks Modified Proton Exchange Membranes for Improving Transport Properties

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Preparation of SPEEK. SPEEK was obtained through the post-sulfonation of PEEK: PEEK pellets (18.0 g) were dispersed into sulfuric acid solution (98 wt%, 138 mL) at room temperature. The mixture was firstly stirred vigorously at room temperature to dissolve PEEK pellets. Then, the reaction mixture was stirred at 45 °C for 5.5 h. Subsequently, the reaction mixture was cooled to room temperature and added into ice water with continuous agitation. The precipitated SPEEk was washed with water until the pH of 7.0, and then dried at room temperature for 48 h 60 °C for 36 h under vacuum. The degree of sulfonation of the SPEEK was obtained by ^{1}H NMR spectrum of it. The degree of sulfonation (DS) of as-prepared SPEEK could be quantitatively determined based on the following formulas:

$$\frac{n}{12-2n} = \frac{A_{H_E}}{\sum A_{H_{AA^*BB^*CD}}}$$

$$\mathrm{DS} = n \times 100\%$$

where A_{H_E} is the peak area of the distinct H_E signals, $\sum A_{H_{AA^*BB^*CD}}$ is the intergrated areas of the signals related to all the other aromatic hydrogens. The DS was calculated to be 62%.

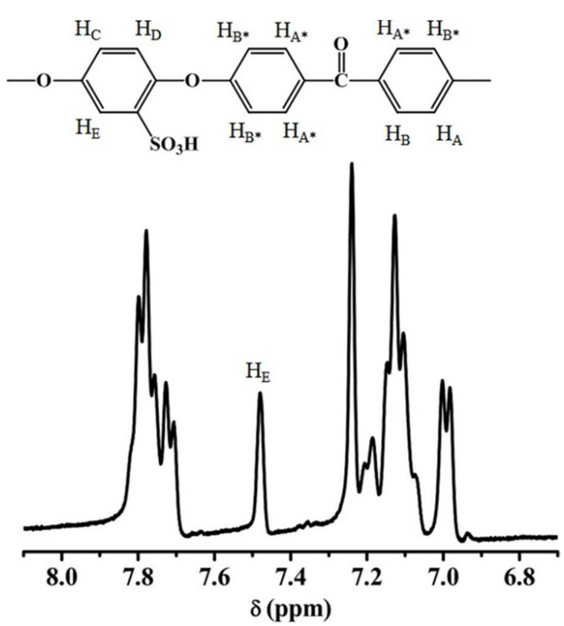

Figure S1. ^{1}H NMR spectrum of as-prepared SPEEK sample.

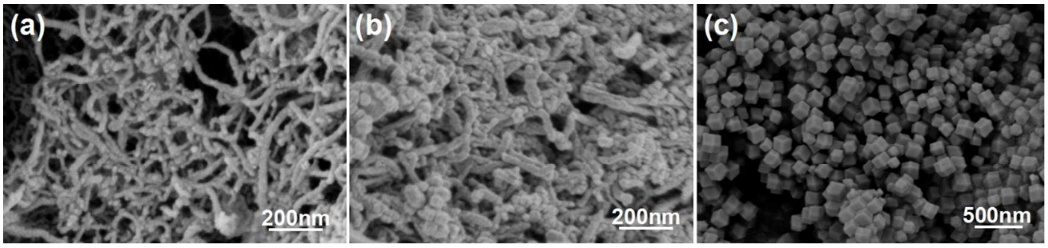

Figure S2. SEM images of CNT (a), ZCN (b) and ZIF-8 (c).

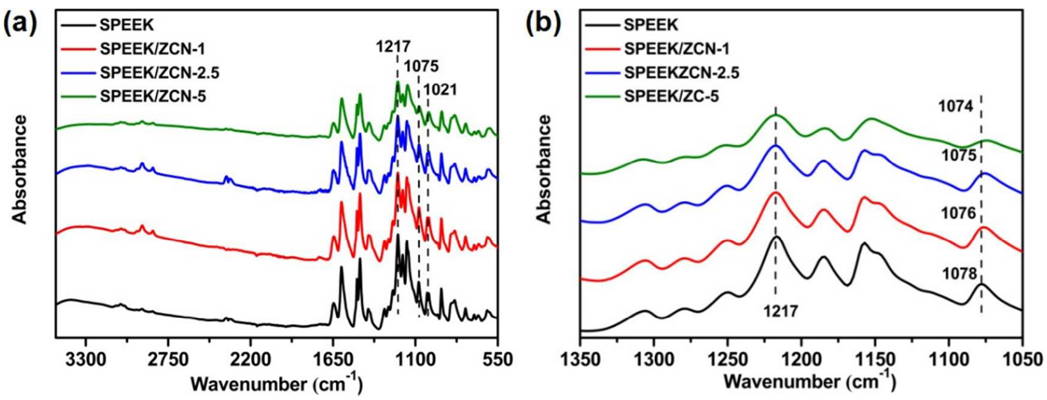

Figure S3. FTIR spectra of the recast SPEEK membrane and SPEEK/ZCN composite membranes (a); The corresponding FTIR spectra of these membranes in the wavenumber range of 1350 cm^{-1} to 1050 cm^{-1} (b).

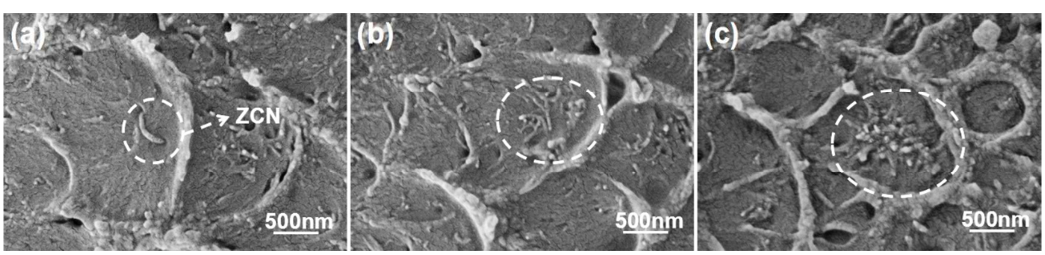

Figure S4. Cross-sectional SEM images of the SPEEK/ZCN-0.5 (a), SPEEK/ZCN-2.5 (b) and SPEEK/ZCN-5 (c) composite membranes at higher magnification.

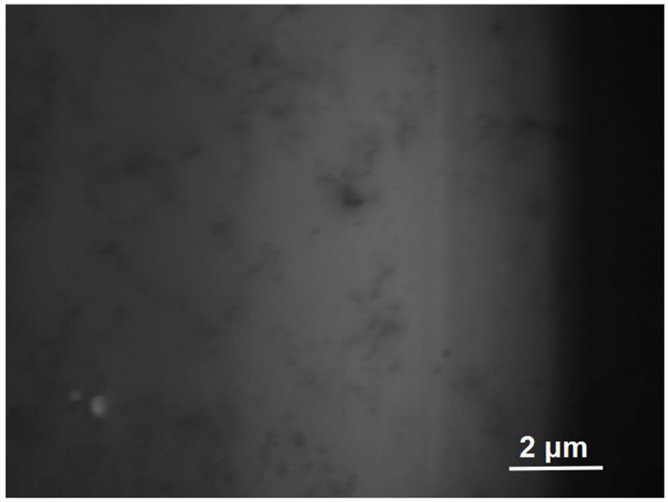

Figure S5. Cross-sectional TEM image of the SPEEK/ZCN-2.5 composite membrane.

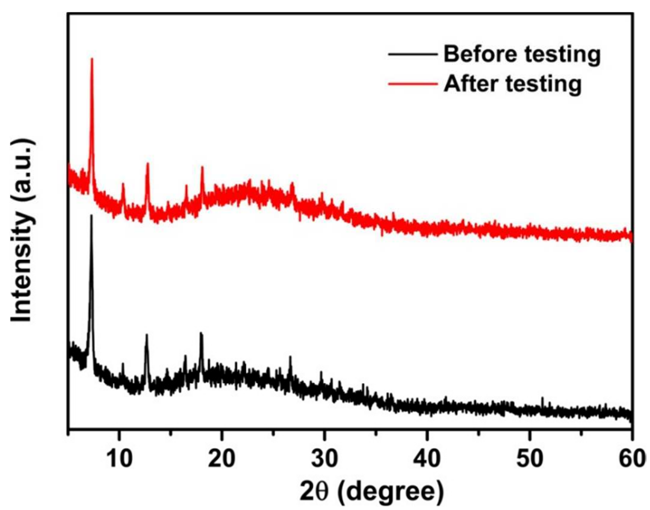

Figure S6. XRD curves of the SPEEK/ZCN-10 composite membrane before and after proton conductivity test.

Table S1. Mechanical properties of the recast SPEEK and SPEEK/ZCN composite membranes

Samples	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SPEEK	39.3	1291	48.3
SPEEK/ZCN-1	43.1	1475	42.3
SPEEK/ZCN-2.5	50.8	1853	27.1
SPEEK/ZCN-5	58.3	2132	12.5

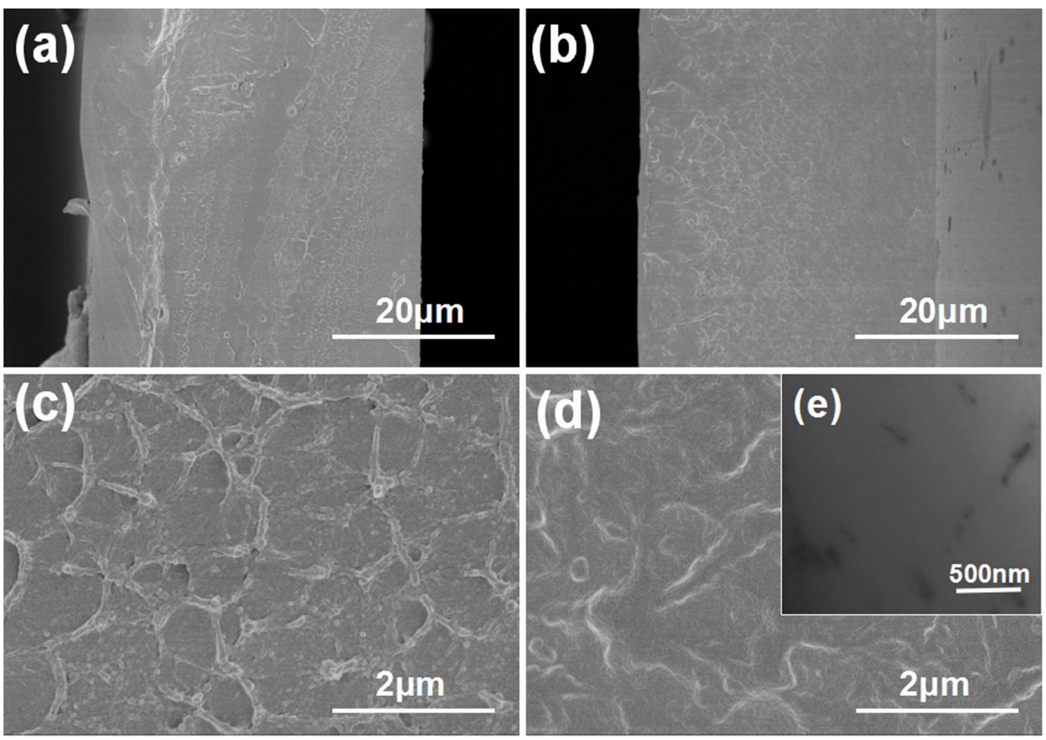

Figure S7. Cross-sectional SEM images of the SPEEK/ZIF (a, c) and SPEEK/ZC (b, d) composite membranes; Cross-sectional TEM image of the SPEEK/CNT composite membrane (e)

Table S2. Comparison of transport properties of SPEEK/ZCN-2.5 composite PEM with other reported SPEEK-based PEMs.

PEMs	Proton Conductivity (S cm^{-1})	High-humidity Conditions	Proton Conductivity (mS cm^{-1})	Low-humidity Conditions	Reference
SPEEK/SRGO-1.0	0.12	80 °C-100 % RH	8.6	80 °C-50 % RH	1
SPEEK/SSGO-10	0.07	65 °C-100 % RH	4.5	145 °C-0 % RH	2
SPEEK/BPO_4@CNTs-2	0.21	80 °C-100 % RH	-	-	3
SP/ABC	0.09	85 °C-100 % RH	0.8	145 °C-0 % RH	4
SPEEK/ZPMA-10	0.08	80 °C-100 % RH	-	-	5
SP/NF-NH_2	0.093	65 °C-100% RH	27.0	120 °C-2 % RH	6
SPEEK/ZCN-2.5	0.206	70 °C-100 % RH	50.24	120 °C-30 % RH	This work

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