Ultrathin proton exchange membranes with enhanced dimensional stability towards acidic CO_2 electroreduction

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Experimental Section

Chemicals and Materials

$Cu(NO_3)_2 \cdot 3H_2O$, H_2SO_4 (98%), $AgNO_3$, K_2SO_4, N,N-dimethylformamidex (DMF) and ethanol, hydrazine hydrate, polyvinyl pyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanolamine was purchased from Acros Organics. 1,3,5-benzenetricarboxylic acid (BTC) and poly(ether ether ketone) (PEEK) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Porous polycarbonate substrate (200 nm) was purchased from Whatman. The ultrapure water with 18.2 MΩ used through the experiments was prepared by Millipore pure water system.

The sulfonation of PEEK

PEEK powders were heated at 120 ℃ overnight to remove adsorbed water, and then dispersed in H_2SO_4 (98%) with various stirring at 60 ℃ for 6 h. The SPEEK was recovered by precipitating the acid solution into excess a mixture of water and ice. The SPEEK was wash with water for several times until the pH reached 7. Finally, the as-prepared SPEEK was dried in a vacuum oven for 24 h.

The preparation of Ag nanoparticles (Ag NPs)

The Ag nanoparticles were prepared by the method reported previously.[S1] Generally, 10 mL $AgNO_3$ solution was dropped into 50 mL 2% PVP solution and stirred for 2h. Then 3 mL 5% hydrazine hydrate was added

into the above solution and stirred for 5 min to obtain Ag NPs. After washing with deionized for several times to remove PVP, Ag NPs were ready for usage.

The synthesis of MIL-110 nanoneedle skeletons

The MIL-110 nanoneedle skeletons were prepared by scarifying copper hydroxide nanostrands (CHNs).[S2] CHNs were synthesized by mixing equal volume 4 mM $Cu(NO_3)_2$ solution and 1.4 mM ethanolamine solution and aging for 2 days. The obtained CHNs were filtered onto a porous PC membrane (diameter, 2 cm) and transferred carefully onto an Al foil surface with the assistance of ethanol. Then the Al foil with CHNs were soaking in 1 mM BTC solution and heated at 120 ℃ for 24 h to form the MIL-110 nanoneedle skeletons.

The preparation of MIL-110@SPEEK membranes

SPEEK was dissolved into DMF to prepare dilute solutions with a series of concentrations of 0.10, 0.15, 0.20 and 0.25 g mL^{-1}. 0.1 mL diluted SPEEK solution was dropped onto the surface of MIL-110 skeletons, followed by spinning at 1000 rpm for 20 s. Then a negative pressure treatment was conducted to remove the gas in the MIL-110 skeleton and to fill SPEEK into the porous structure. The hybrid membrane was heated at 60 ℃ for 6 h to obtain MIL-110@SPEEK membranes. Finally, the Al foil with MIL-110@SPEEK was treated in 1 M HCl solution and MIL-110@SPEEK was carefully peeled off to achieve the free-standing

membrane. According to the applied SPEEK concentrations, the hybrid membranes were named as MIL-110@SPEEK-0.10, MIL-110@SPEEK-0.15, MIL-110@SPEEK-0.20 and MIL-110@SPEEK-0.25, respectively.

Material Characterizations

The crystal phase of the samples was tested by powder X-ray diffraction (XRD) using an X'Pert PRO (XRD6100, Shimadzu) with Cu Kα radiation at room temperature with a step of 0.02 degrees. The scanning electron microscopy (SEM) (JSM-IT800) equipped with energy-dispersive spectroscopy (EDS) (Oxford) was applied to test the morphology and elements distribution of the SPEEK and hybrid membranes. Fourier transform infrared spectroscopy (FT-IR) was recorded on FT-IR TENSOR 27 equipment in the range of 500-2000 cm^{-1}. X-Ray photoelectron spectra (XPS) were recorded on Krato AXISSUPRA. The thermogravimetry analysis (TG) of the membranes with temperature from 50 ℃ to 750 ℃ was measured by TA-Q500b at a ramp rate of 10 °C/min under N_2 atmosphere. Before TG test, the membrane samples were soaking in 0.1 M H_2SO_4 aqueous solution overnight to do the ion exchange and active the membranes. After that, the samples were taken out and dried in air at room temperature for 24 h. Then, the samples were stored at 50 ℃ for 30 min, followed by the heating process to 750 ℃. The mechanical property of the membranes was recorded by Universal Testing Machine (Wu Jia Machine,

WJ-LL-200).

The water uptake (UP) and swelling ratio (SW) under various temperatures were tested. The membranes were cut into rectangular strips, the dry weight (W_{dry}) and dry dimensiona (L_{dry}) of which were recorded, and immersed in deionized water at a certain temperature for 24 h. Then the wet weight (W_{wet}) and weight dimension (L_{wet}) were measured after removing excess water. The WU and SW were calculated by the following formulas:

$$WU\ (\%) = (W_{wet} - W_{dry})/W_{dry} \times 100\%$$

$$SR\ (\%) = (L_{wet} - L_{dry})/L_{dry} \times 100\%$$

The ion exchange capacity (IEC) was evaluated by the titration method. The membrane was completed in a saturated NaCl solution for 24 h. Then the solution was titrated with 0.01 M NaOH to obtain the H^+ concentration. The IEC was calculated by the following formula:

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

Where, C_{NaOH} and V_{NaOH} represented the concentration and volume of NaOH solution.

The proton conductivity of the membranes was tested by the electrochemical impedance spectra (EIS) using electrochemical workstation (CHI 660E) with the frequency range from 1 MHz to 1 Hz at AC amplitude of 0.5 V. The membrane was soaked in 0.1 M H_2SO_4 solution for 24 h before test. After wiping excess solution, the membranes

were placed in the temperature humidity test chamber under a constant temperature and humidity overnight. Then, a two-electrode system was conducted to test the proton conductivity. The resistance (R_{ct}) of the membrane was calculated based on the EIS. The proton conductivity (σ) was obtained through the following formula:

$$\sigma = L / (R_{ct}S)$$

where, L referred to the length between two electrodes, S referred to the area of the cross-section of the membrane.

The CO_2 electroreduction performance was tested in a flow cell. Rectangular carbon paper (Suzhou Sinero Technology Co., Ltd.) with size of 2.5 cm × 1 cm was washed with ethanol and ultrapure water and purged with Ar. 20 mg Ag NPs were dispersed into the mixture of 0.3 mL ethanol, 0.2 mL ultrapure water and 10 μL 5% Nafion. The gas diffusion electrodes were prepared by drop-coating. 0.5 mL Ag NPs dispersion onto the carbon paper surface and being dried at 60 ℃ in vacuum. The CO_2 electroreduction test was conducted in a three-electrode system by an electrochemical workstation (CHI660E). The gas electrode was applied as the working electrode, and Ag/AgCl electrode as the reference electrode, Pt as the counter electrode and 0.5 M K_2SO_4 (pH=2, regulated by H_2SO_4) as electrolyte. The remnant air in the cell was removed by purging pure N_2 and CO_2 for 30 min before the test. Then, CO_2 was purged at a constant flux for electrolysis test, with the electrolyte cycling at the rate of 0.1 mL

min^{-1}. The gas products were analyzed by gas chromatograph (GC-2014, Shimadzu).

Figures

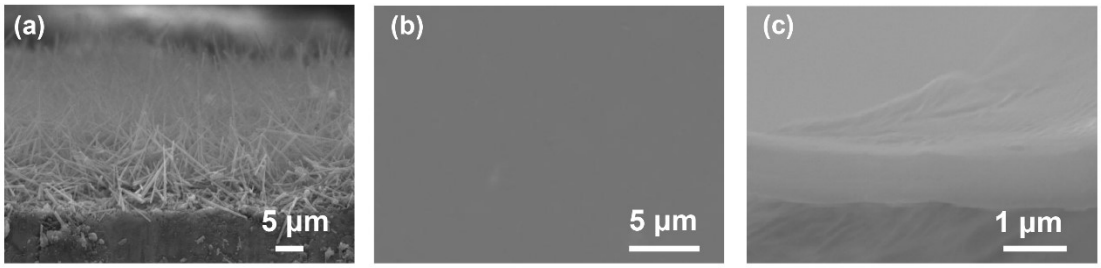

Fig. S1. The SEM images of (a) the cross-section of MIL-110 skeletons, (b) the surface and (c) the cross-section of the SPEEK membrane.

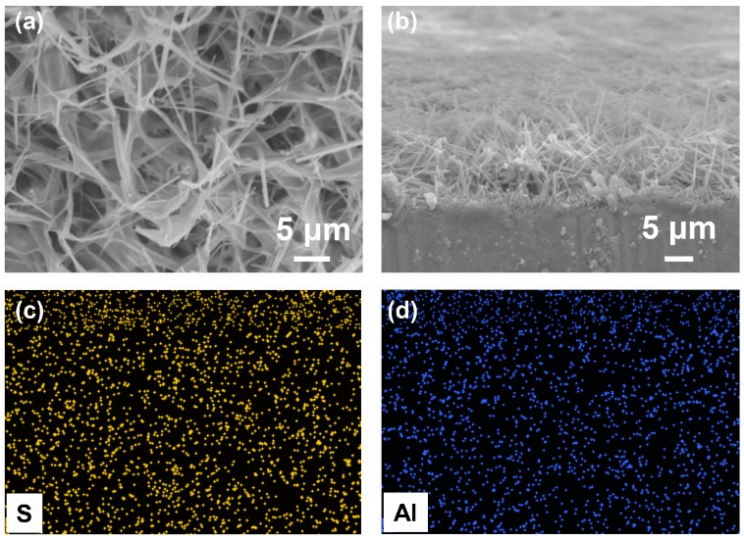

Fig. S2. The SEM images of (a) the surface and (b) the cross-section of the MIL-110@SPEEK-0.10. The EDS mapping of (c) S element and (d) Al element in (a).

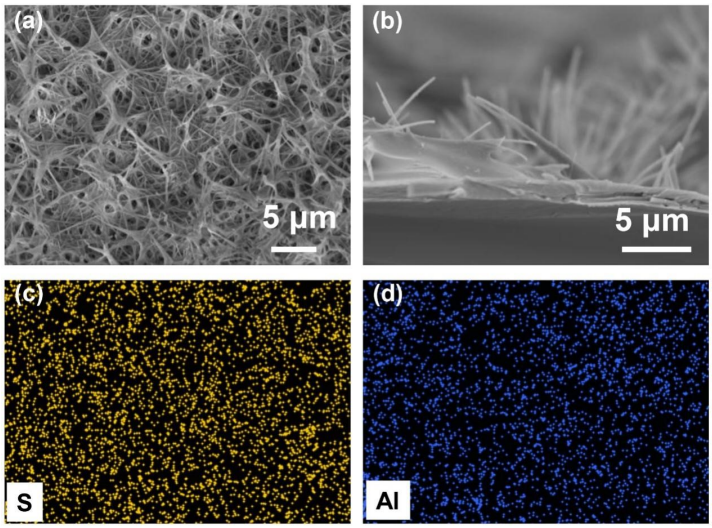

Fig. S3. The SEM images of (a) the surface and (b) the cross-section of the MIL-110@SPEEK-0.15. The EDS mapping of (c) S element and (d) Al element in (a).

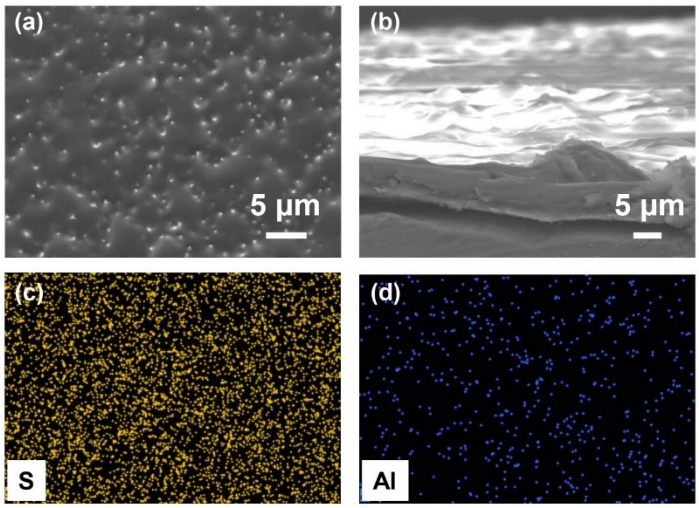

Fig. S4. The SEM images of (a) the surface and (b) the cross-section of the MIL-110@SPEEK-0.25. The EDS mapping of (c) S element and (d) Al element in (a).

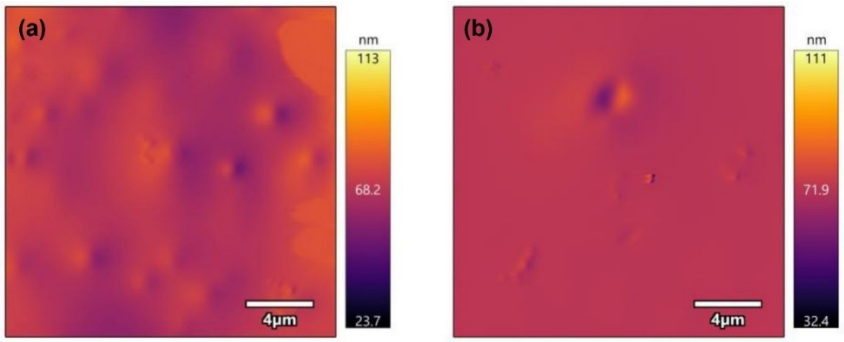

Fig. S5. The AFM images of (a) the MIL-110@SPEEK-0.20 and (b) MIL-110@SPEEK-0.25 membranes.

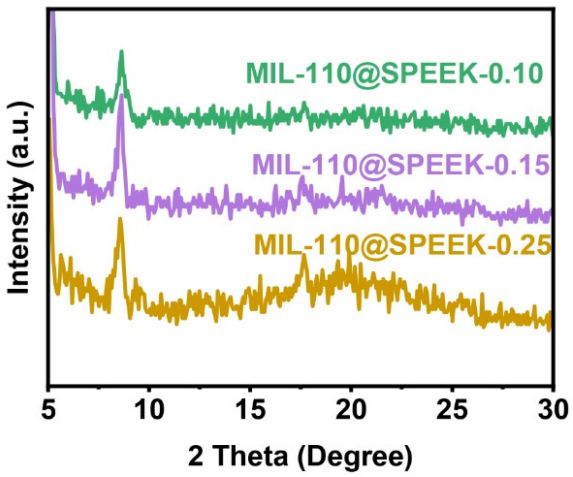

Fig. S6. The XRD patterns of MIL-110@SPEEK membranes.

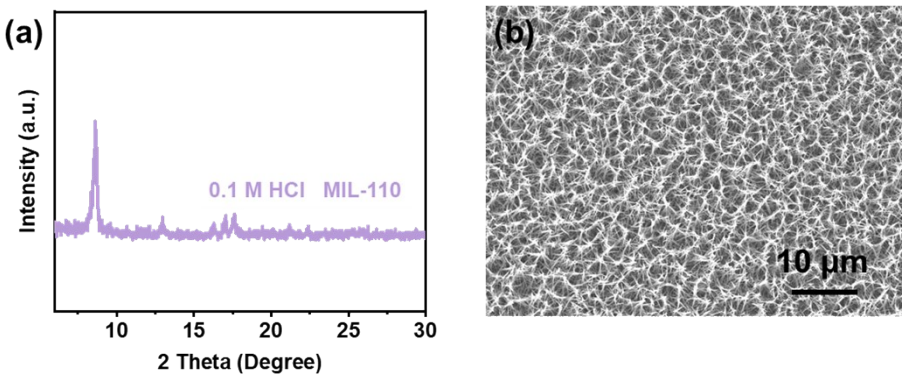

Fig. S7. (a) The XRD pattern and (b) SEM image of the MIL-110 skeleton which was treated in 0.1 M HCl solution for a week.

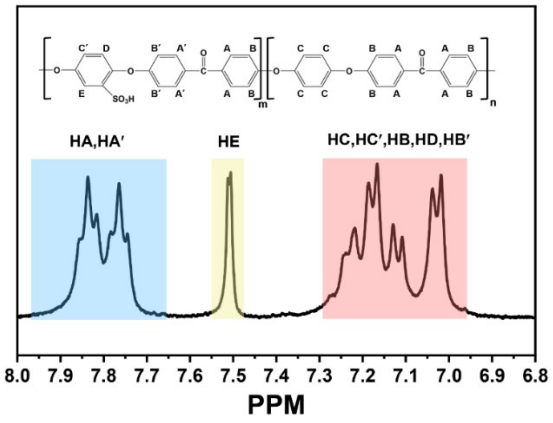

Fig. S8. The ^{1}H NMR spectra of SPEEK.

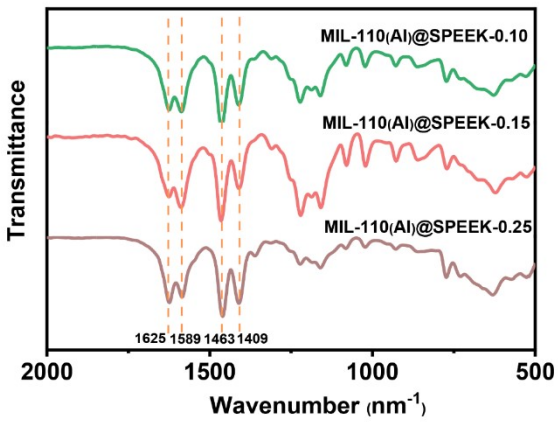

Fig. S9. The FTIR curves of MIL-110@SPEEK membranes.

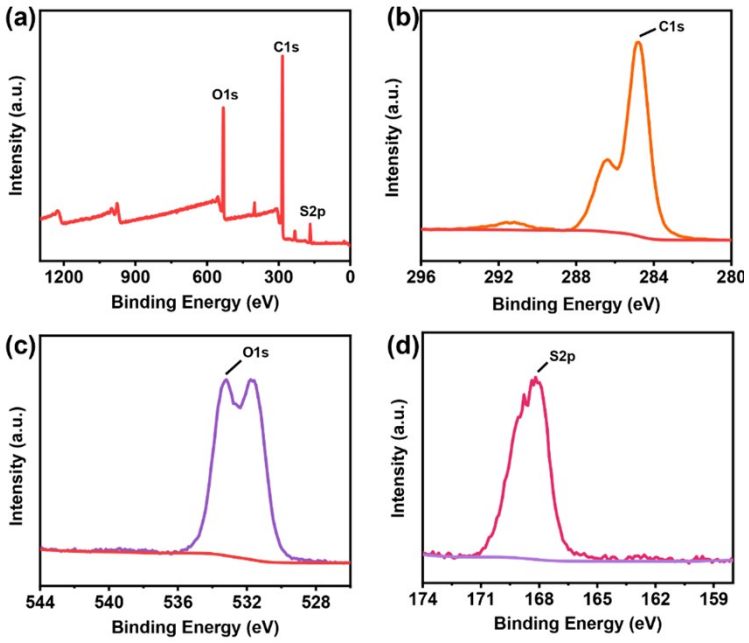

Fig. S10. The XPS (a) survey, (b) C 1s, (c) O 1s and (d) S 2p spectra of the SPEEK membrane.

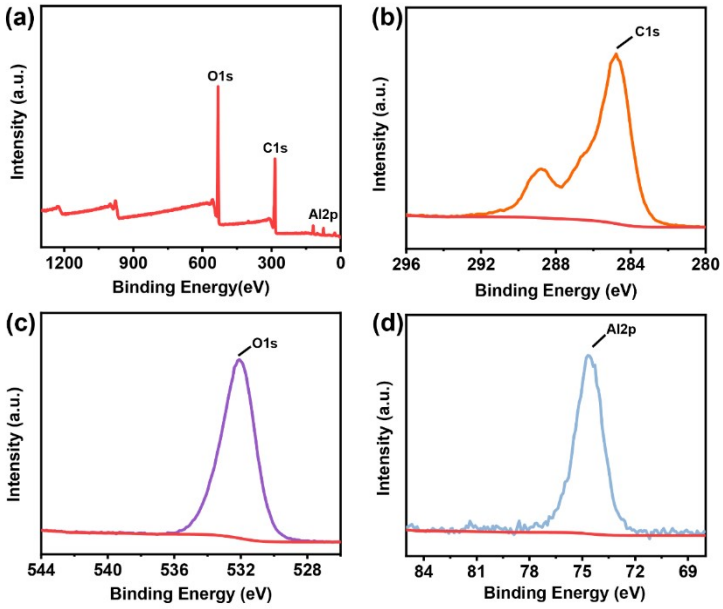

Fig. S11. The XPS (a) survey, (b) C 1s, (c) O 1s and (d) Al 2p spectra of the MIL-110 skeletons.

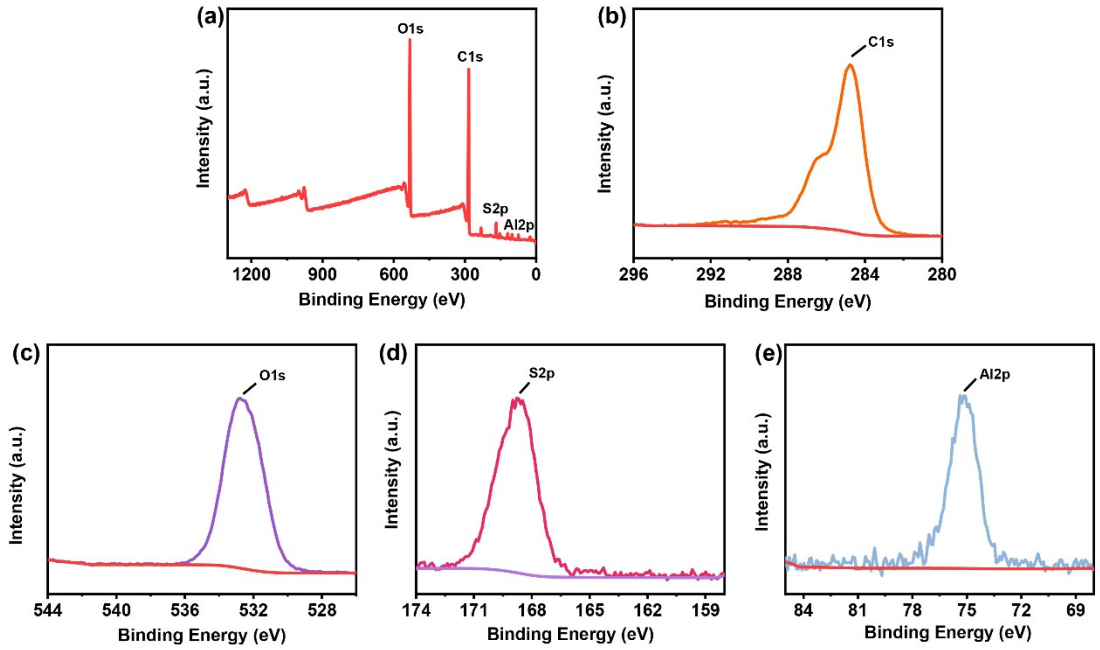

Fig. S12. The XPS (a) survey, (b) C 1s, (c) O 1s, (d) S 2p and (e) Al 2p spectra of the MIL-110@SPEEK-0.10 membrane.

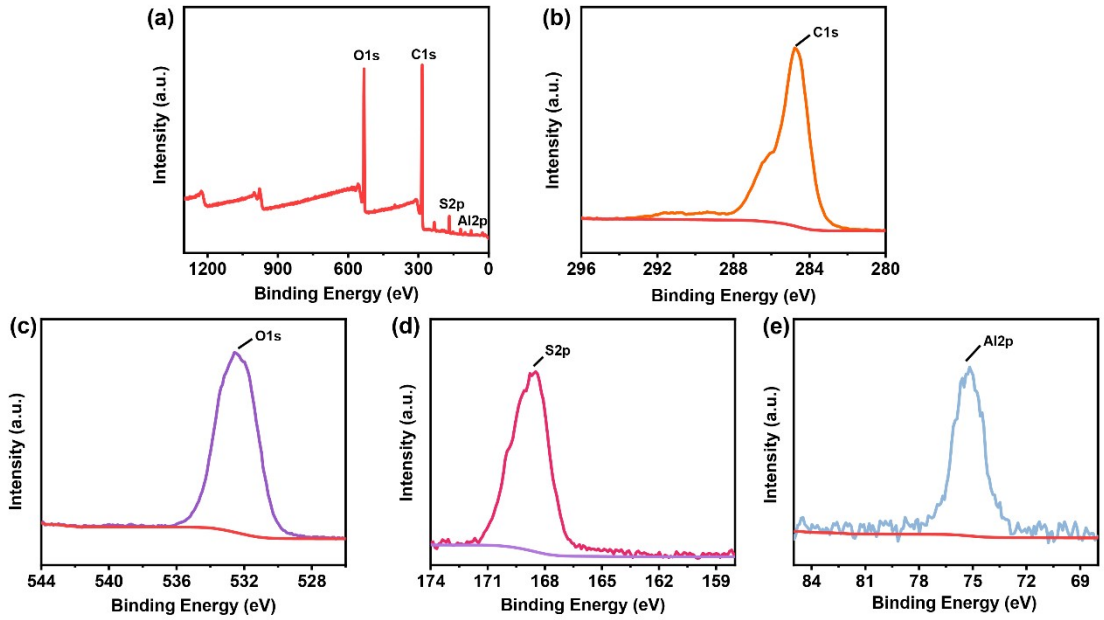

Fig. S13. The XPS (a) survey, (b) C 1s, (c) O 1s, (d) S 2p and (e) Al 2p spectra of the MIL-110@SPEEK-0.15 membrane.

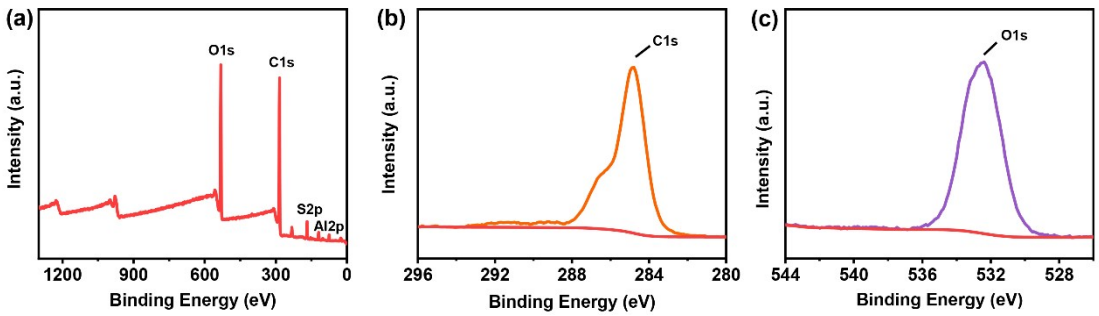

Fig. S14. The XPS (a) survey, (b) C 1s and (c) O 1s spectra of the MIL-110@SPEEK-0.20 membrane.

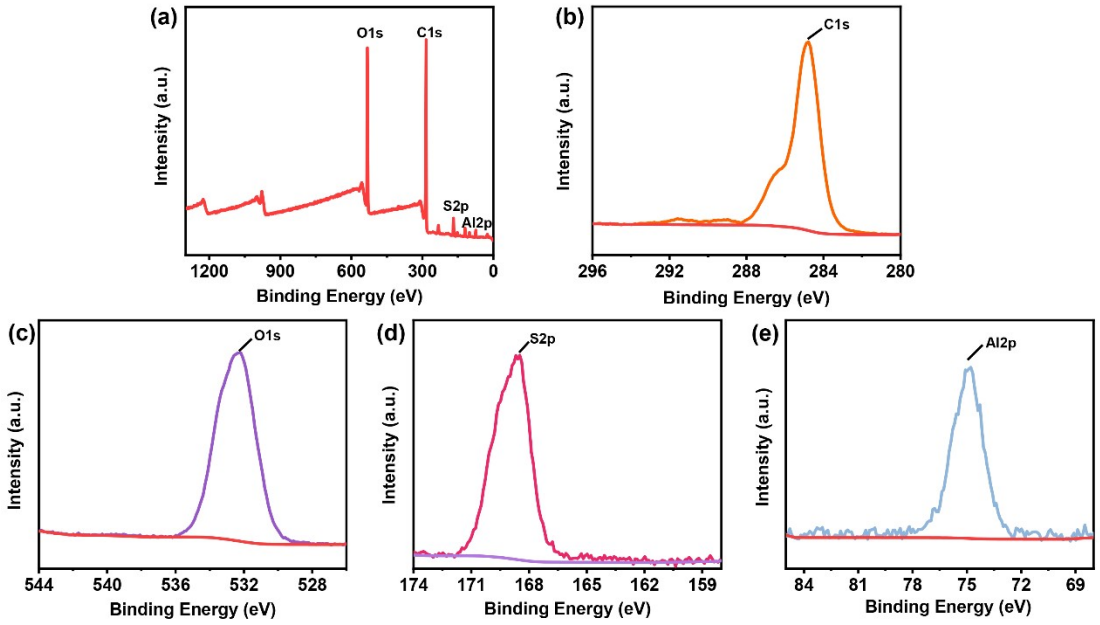

Fig. S15. The XPS (a) survey, (b) C 1s, (c) O 1s, (d) S 2p and (e) Al 2p spectra of the MIL-110@SPEEK-0.25 membrane.

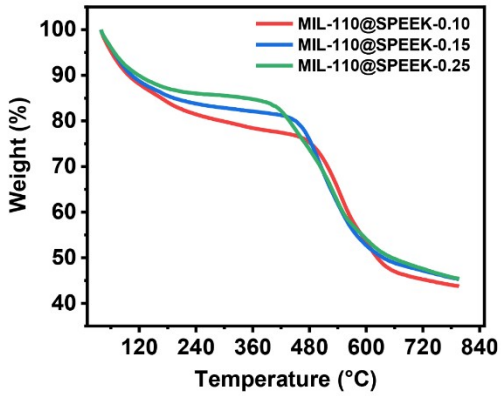

Fig. S16. The TG curves of MIL-110@SPEEK membranes.

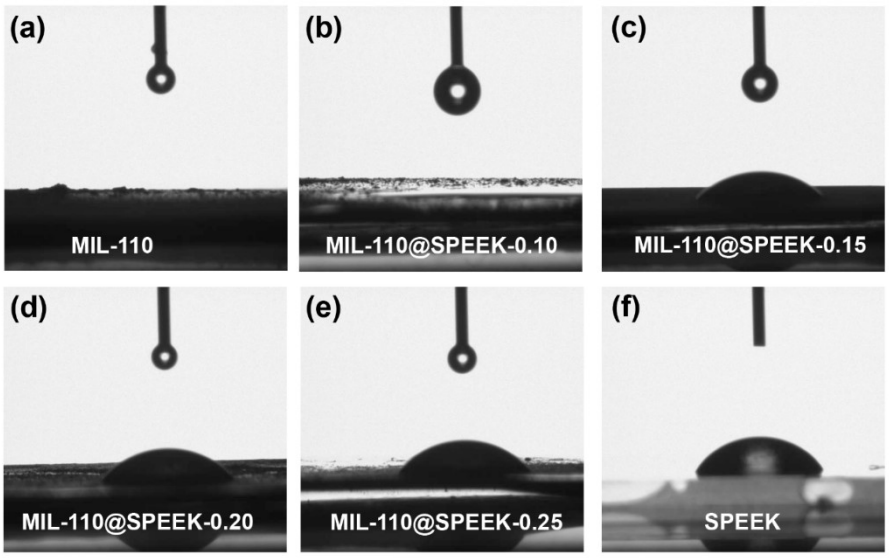

Fig. S17. The contact angles of SPEEK, MIL-110 and MIL-110@SPEEK membranes.

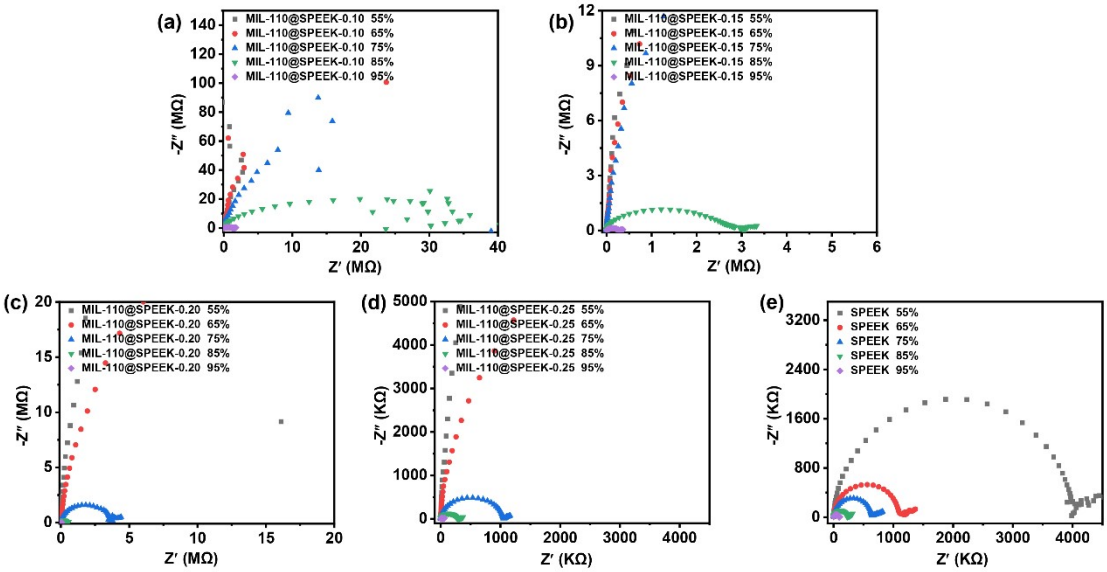

Fig. S18. The EIS of MIL-110@SPEEK and SPEEK membranes under various humidities.

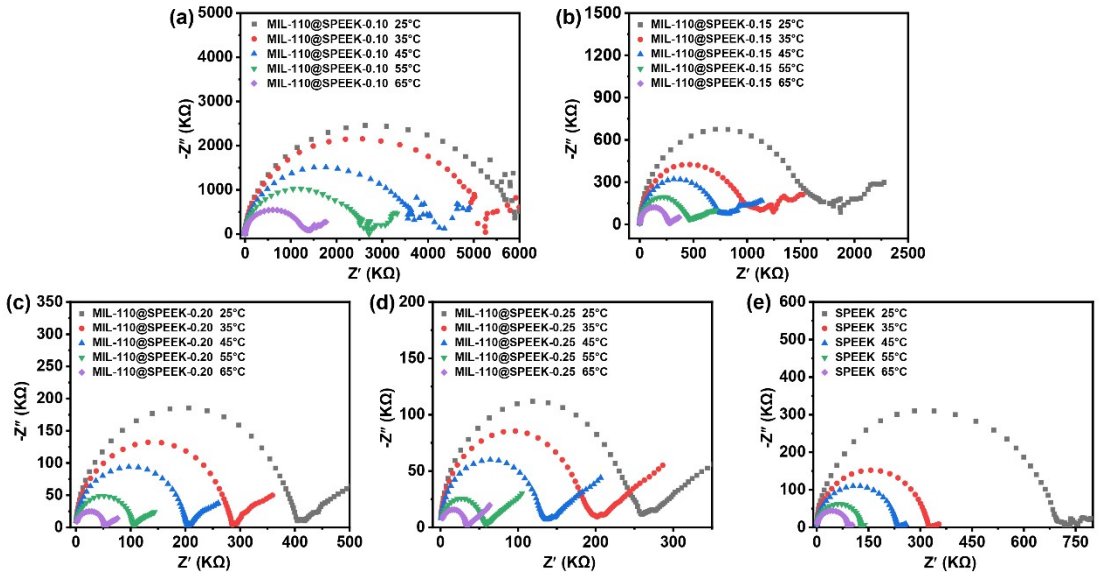

Fig. S19. The EIS of MIL-110@SPEEK and SPEEK membranes under various temperatures.

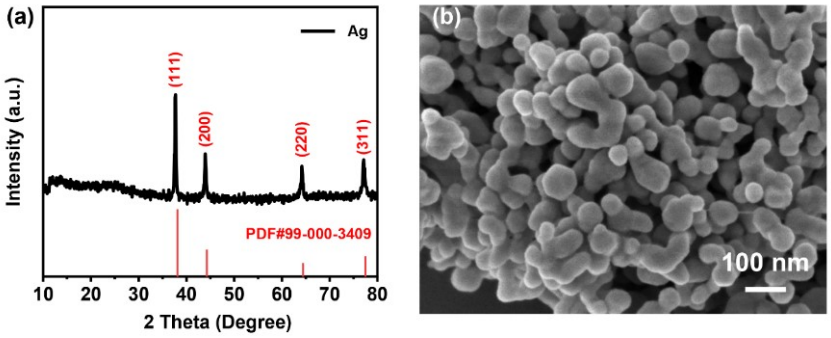

Fig. S20. (a) The XRD pattern and (b) SEM image of Ag nanoparticles.

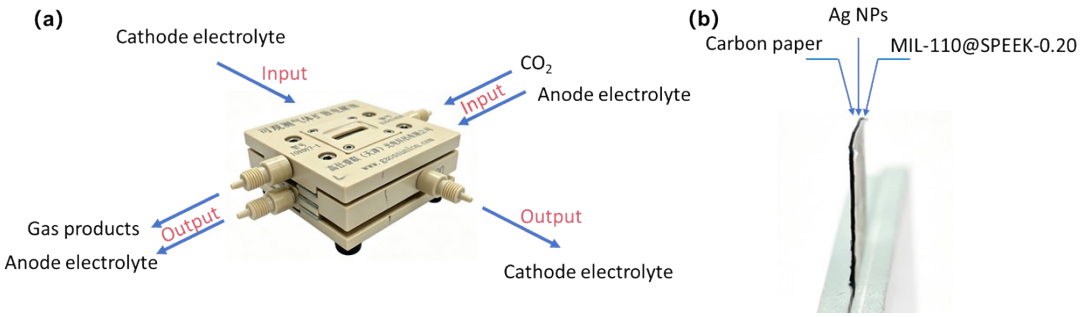

Fig. S21. The photos of (a) the flow cell for acidic CO_2 electroreduction and (b) the gas diffusion electrode.

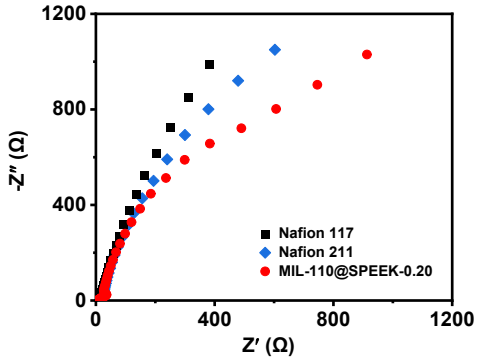

Fig. S22. The EIS of the cell with Nafion 117, Nafion 211 or MIL-110@SPEEK-0.20 membrane.

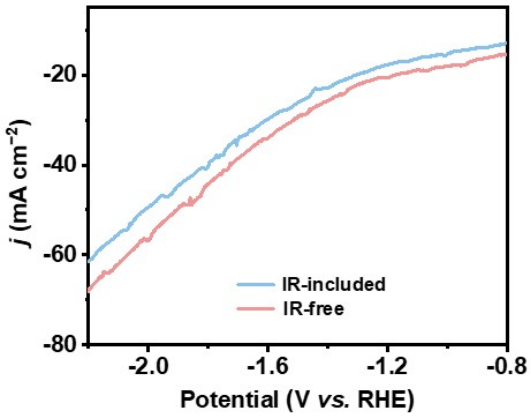

Fig. S23. The IR-free and IR-included IV curves of the cell with MIL-110@SPEEK-0.20 membrane.

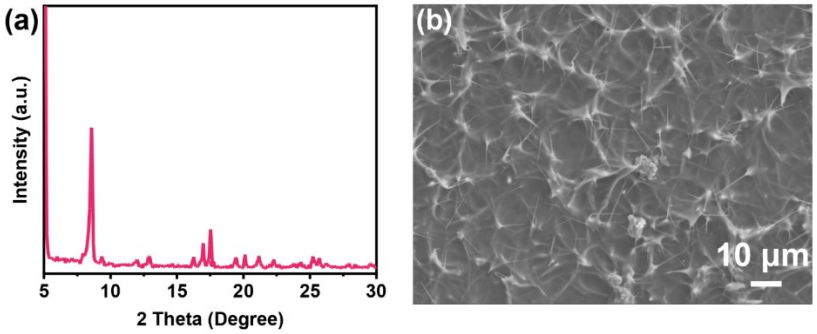

Fig. S24. The XRD pattern and SEM image of the MIL-110@SPEEK-0.20 membrane after working.

References

S1 P. Zhu, Y. Guo, Y. Zhang, S. Wu, R. Wang, Z. Si, X. She, Y. Deng and Q. Yu, *Inorg. Chem.*, 2026, **65**, 6402-6411.

S2 Y. Mao, H. Huang, Y. Liu, L. Shi, W. Cao, J. Li, L. Sun and X. Peng, *CrystEngComm*, 2013, **15**, 5591.