Supplementary Information

Water-confined CuFe Prussian blue analogues empower Nafion membranes for high-temperature/low-humidity fuel cells

Jun Zhang[a], Yalin Fan[a], Jinqiu Ye[a], Changming Zhong[a], Liangyu He[a], Xuan Zhou[a], Yu Liu[a], Ce Wang[b], Ping Hu[c], Yong Liu[a,*]

[a] Beijing Key Laboratory of Advanced Functional Polymer Composites, College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.
[b] Alan G. MacDiarmid Institute, Jilin University, Changchun, Jilin 130012, China.
[c] Department of Chemical Engineering, Tsinghua University, Beijing 100084, China.

E-mail: yongliu@mail.buct.edu.cn (Y. Liu).

Experimental section

1. Materials

Nafion resin pellets (NR40) were obtained from DuPont, USA. Copper nitrate ($Cu(NO_3)_2$, >98%), potassium ferricyanide ($K_3[Fe(CN)_6]$, >98%), and sodium citrate ($C_6H_5Na_3O_7$, >98%) were sourced from Shanghai Macklin Biochemical Co., Ltd., China. N,N-dimethylformamide (DMF, analytical grade), sodium hydroxide (NaOH, analytical grade), hydrogen peroxide (H_2O_2, 6% solution), sulfuric acid (H_2SO_4, 98%), and anhydrous ethanol (analytical grade) were purchased from Beijing Tongguang Fine Chemicals Co., Ltd., China. Gas diffusion layer electrodes (GDE, Pt 0.5 mg cm^{-2}) were obtained from Johnson Matthey. Phenolphthalein solution and deionised water were prepared in the laboratory. All chemicals were used as supplied without further purification.

2. Preparation of CuFe-PBA Framework Materials

Copper Prussian blue analogues (CuFe-PBA) were synthesised through a chemical co-precipitation method. First, a specific amount of $Cu(NO_3)_2{\cdot}xH_2O$ and 1 mmol of sodium citrate were co-dissolved in 20 mL of deionised water. To produce compounds with different morphologies or properties, the amount of $Cu(NO_3)_2$·xH2O was adjusted to 1.1 mmol, 1.35 mmol, 1.65 mmol, and 2.25 mmol (corresponding to the products named CuFe-PBA-1, CuFe-PBA-2, CuFe-PBA-3, and CuFe-PBA-4, respectively). After the solids had fully dissolved, 20 mL of a 0.02 M $K_3[Fe(CN)_6]$ solution was loaded into a syringe pump and injected over 30 minutes. Continuous stirring was maintained during injection to ensure a homogeneous reaction. The mixture was then left to react at 25 °C for 24 hours. The final products were separated by centrifugation, thoroughly washed 2–3 times with deionised water, and dried in a vacuum oven at 60 °C to obtain the final CuFe-PBA-x (x = 1–4) samples.

3. Preparation of Nafion Casting Solution

First, 4 g of Nafion resin pellets were weighed and fully immersed in a mixed solvent consisting of 80 mL of absolute ethanol and 16 mL of deionised water. Subsequently, the mixture was transferred into a high-pressure autoclave fitted with magnetic stirring and reacted in a sealed environment at 160 °C and 400 rpm for 4 hours. After the autoclave cooled naturally to room temperature, a homogeneous and transparent Nafion water-alcohol solution with a mass fraction of 5% was obtained. Next, 20 mL of the prepared Nafion solution was accurately measured, and 2 mL of N,N-dimethylformamide (DMF) was slowly added dropwise as a high-boiling-point solvent. Finally, the mixture was subjected to thorough ultrasonication to ensure uniform dispersion, resulting in the final Nafion casting solution.

4. Preparation of CuFe-PBA/Nafion Composite Membranes

The pre-dispersed CuFe-PBA solution was mixed with 5 mL of the Nafion casting solution, stirred mechanically for 4 hours, and then subjected to ultrasonication. A polytetrafluoroethylene (PTFE) plate was placed on a horizontal heating stage. A small amount of the CuFe-PBA/Nafion casting solution was added dropwise to thoroughly wet the PTFE plate, followed by the addition of the remaining casting solution. After casting at room temperature for 12 hours, the membrane was dried at 60 °C for 10 hours to ensure complete solvent evaporation. Finally, the composite membrane was heat-treated at 130 °C for 2 hours to produce the final proton exchange membrane (PEM). The composite membrane was fully activated in a 0.5 mol L^{-1} sulfuric acid solution for 24 hours, washed with deionised water until neutral, and dried for further use. This was denoted as x wt%-CuFe-PBA/Nafion (where x indicates the mass fraction of the filler relative to the membrane). The pristine Nafion membrane was prepared using the same procedure. The thicknesses of all prepared composite membranes were maintained within the range of 50-55 μm.

5. Structural and Morphological Analysis of CuFe-PBA

The crystal structure of the CuFe-PBA powder samples was examined using an X-ray diffractometer (XRD, Rigaku-2038, Rigaku, Japan) with a scanning rate of 10 °/min over a 2θ range of 10° to 80°. The characteristic functional groups of the samples were identified using a Fourier transform infrared spectrometer (FT-IR, Fisher Scientific Nicolet iS20, Thermo, USA) within a scanning range of 400 to 4000 cm^{-1}. The surface elemental composition and the chemical valence states of the transition metals were characterised by X-ray photoelectron spectroscopy (XPS, Nexsa G2, Thermo, USA). All binding energy data were calibrated against the adventitious carbon C 1s peak (284.8 eV) as a reference.

For micromorphological observations, the samples were routinely sputter-coated with gold, and their surface morphology and particle distribution were examined using a scanning electron microscope (SEM, Sigma 360, ZEISS, Germany). To further investigate the internal structure and lattice features, high-resolution observations were performed with a transmission electron microscope (TEM, Talos F200x, FEI, USA). The thermal stability of CuFe-PBA was evaluated using a thermogravimetric analyser (TGA, STA200, HITACHI, Japan) under a nitrogen atmosphere, heating from room temperature to 400 °C at a rate of 10 °C/min.

6. Performance Characterization of Proton Exchange Membranes

6.1 Mechanical Properties

The mechanical strength of the proton exchange membranes was assessed using a universal tensile testing machine (iDearTest-300, Guangdong Xinke) at a crosshead speed of 5 mm/min, an ambient temperature of 25 °C, and a relative humidity of 50%. The thermal stability of the composite membranes was examined using a thermogravimetric analyser (TGA, STA200, HITACHI, Japan) under a nitrogen atmosphere, heating the samples from 30 °C to 400 °C at a ramp rate of 10 °C/min.

6.2 Ion Exchange Capacity of Proton Exchange Membranes

The ion exchange capacity (IEC) of the composite membranes was quantitatively analysed using a classical acid-base titration method. First, the mass of a thoroughly dried membrane sample was accurately weighed (denoted as W_0). Subsequently, the membrane piece was immersed in a sufficient volume of a 2 M NaCl aqueous solution and left to soak statically at a constant temperature of 30 °C for 48 hours. This step was designed to facilitate the complete exchange of dissociable protons (H^+) within the membrane with Na^+ ions in the solution. After the exchange reaction was complete, several drops of phenolphthalein were added as an indicator to the soaking solution rich in released H^+. The mixture was then titrated with a pre-standardised 0.05 M NaOH solution, and the exact volume of NaOH solution used was recorded (denoted as V_{NaOH}). The IEC value of the membrane sample (in mmol g^{-1}) was calculated according to Equation (1)

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{W_0} \#(1)$$

where C_{NaOH} denotes the molar concentration of the standard NaOH solution (mol L^{-1}); V_{NaOH} indicates the volume of NaOH used to reach the titration endpoint (mL); and W_0 is the mass of the dry membrane before testing (g).

6.3Water Uptake and Swelling Ratio of Proton Exchange Membranes

The water uptake (WU) and swelling ratio (SR) of the composite membranes are key indicators for assessing their dimensional stability and water management capacity under fuel cell operating conditions. Before testing, the dry membrane samples were dried to a constant weight in a vacuum oven. Their initial dry mass (W_0) and initial dimensions (L_0) were accurately measured using an analytical balance and a vernier caliper. The samples were then fully immersed in deionised water within a constant-temperature water bath (80 °C) for 4 hours to ensure adequate swelling. Upon removal, the free water on the surface of the samples was quickly and gently blotted dry with filter paper. Their wet mass (W_1) and dimensions in the fully hydrated state (L_1) were then measured. The WU and SR of the samples were calculated according to Equations (2) and (3), respectively:

$$WU = \frac{W_1 - W_0}{W_0} \#(2)$$

$$SR = \frac{L_1 - L_0}{L_0} \#(3)$$

6.4 Proton conductivity of proton exchange membrane

The proton conductivity (σ) of the composite membranes was measured quantitatively using electrochemical impedance spectroscopy (EIS) with a two-electrode system. During the measurement, the membrane samples were smoothly clamped in a custom-designed polytetrafluoroethylene (PTFE) fixture equipped with two parallel platinum (Pt) electrodes. To assess the humidity dependence of the conduction performance at a constant temperature of 80 °C, the test assembly was placed in airtight chambers containing saturated salt solutions. The relative humidity (RH) was precisely controlled by these specific saturated aqueous solutions; at 80 °C, the saturated solutions of NaCl, NaBr, and $MgCl_2$ provided RH levels of 76%, 51%, and 26%, respectively. An electrochemical impedance analyser (Hioki 3532-80, Hioki, Japan) was used to apply an AC perturbation voltage of 20 mV and record the ohmic resistance of the samples. The proton conductivity was calculated according to Equation (4).

$$\sigma = \frac{l}{t \times w \times R} \#(4)$$

l represents the distance between the two Pt electrodes; t and w denote the thickness and width of the fully hydrated membrane, respectively; and R is the measured ohmic resistance derived from the EIS Nyquist plot.

6.5 Antioxidant Stability of Proton Exchange Membranes

The antioxidant stability of the membranes was tested using Fenton's reagent. Vacuum-dried membrane samples (initial weight, W_0) were immersed in Fenton's reagent (containing 2 ppm Fe^{2+} and 3% H_2O_2) at 80 °C for 2 hours. Afterwards, the samples were thoroughly rinsed, dried, and reweighed (final weight, W_1). The antioxidant stability was determined by calculating the weight loss (W_L) of the membranes.

6.6 Fuel Cell Performance Evaluation

The composite membrane was sandwiched between two gas diffusion electrodes (GDEs) loaded with a Pt/C catalyst (0.5 mg cm^{-2}, Johnson Matthey). An appropriate amount of Nafion solution was sprayed onto the surfaces of the membrane and the electrodes to act as a binder. Subsequently, the assembly was hot-pressed at 130 °C under a pressure of 4 MPa for 4 minutes to produce the membrane electrode assembly (MEA). The prepared MEA was assembled into single-cell hardware and connected to a fuel cell test system. Pure hydrogen (100 mL min^{-1}) and air (500 mL min^{-1}) were supplied to the anode and cathode, respectively, with the gas backpressure on both sides maintained at 150 kPa. The MEA was activated at a constant current density of 400 mA cm^{-2} under 80 °C and 100% relative humidity (RH) for approximately 4 hours until the output voltage stabilised. An electronic load (PLZ-164WA, KIKUSUI, Japan) was used to regulate the output current, and the corresponding steady-state voltage values were recorded to plot the I-V polarization curves of the single cell.

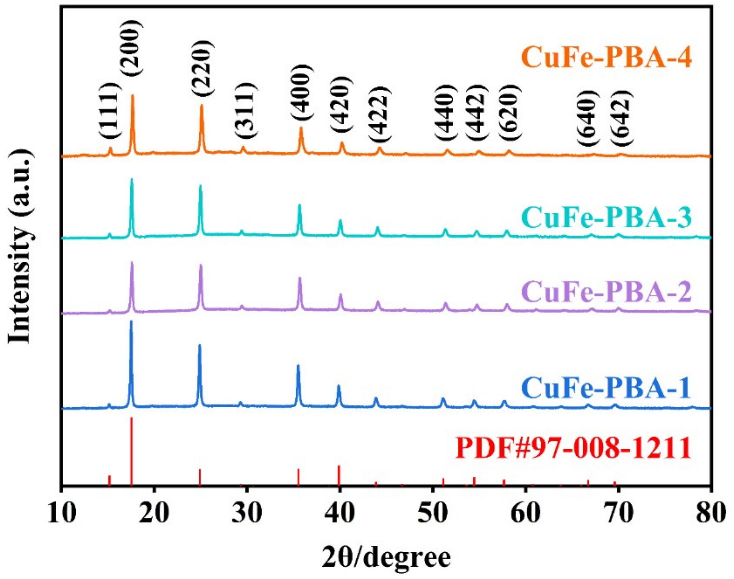

Fig. S1 XRD patterns of CuFe-PBA-x

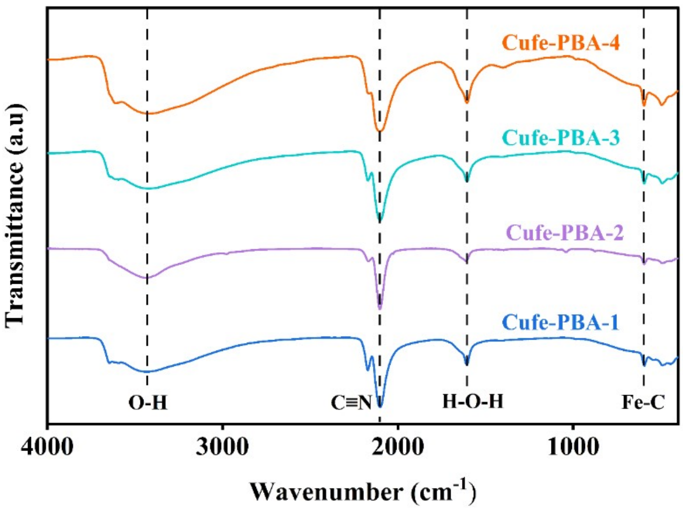

Fig. S2 FT-IR spectra of CuFe-PBA-x

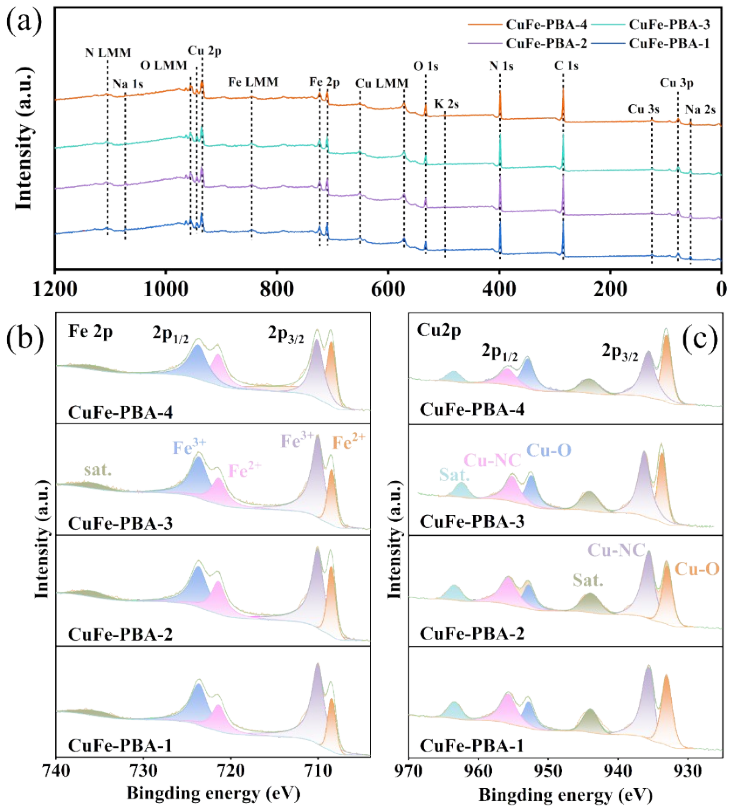

Fig.S3 CuFe-PBA-x (a) XPS survey spectrum, (b) Fe 2p high-resolution spectrum, (c) Cu 2p high-resolution spectrum.

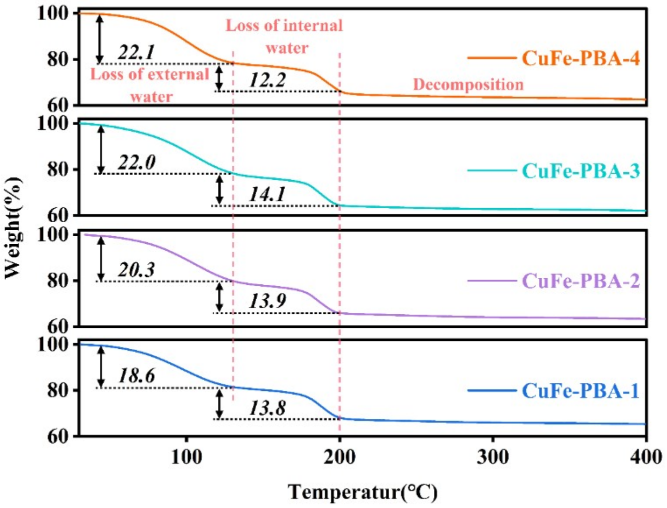

Fig. S4 CuFe-PBA-x thermogravimetric analysis curve

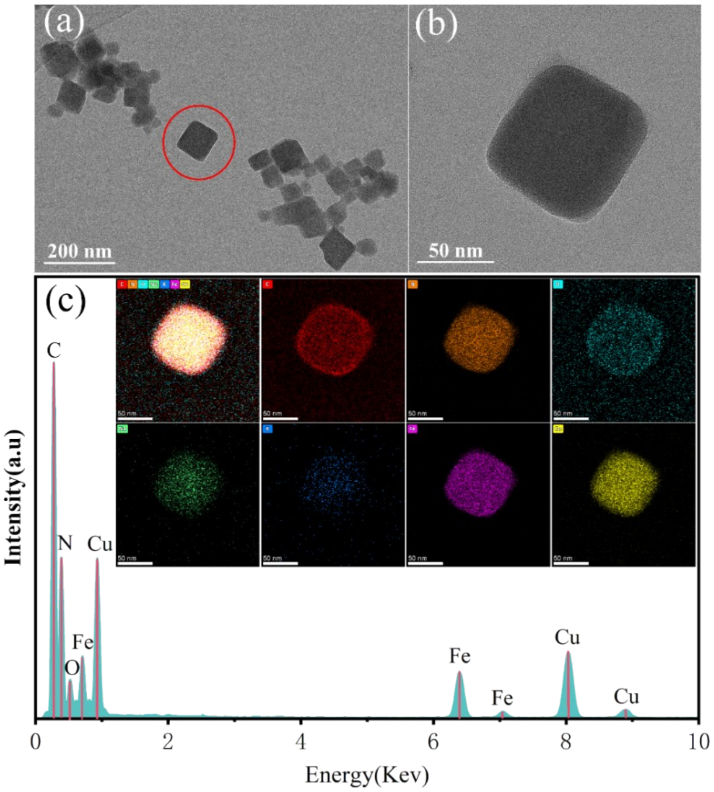

Fig. S5 (a) Low-magnification TEM, (b) High-magnification TEM image of a single particle, (c) Corresponding single-particle EDS elemental mapping image and energy-dispersive X-ray spectroscopy (EDS) quantification curve.

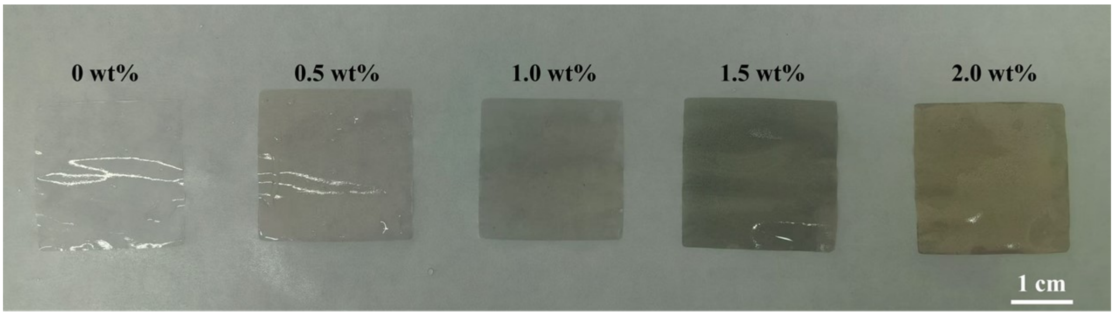

Fig. S6 Digital photographs of x wt%-CuFe-PBA/Nafion composite membranes.

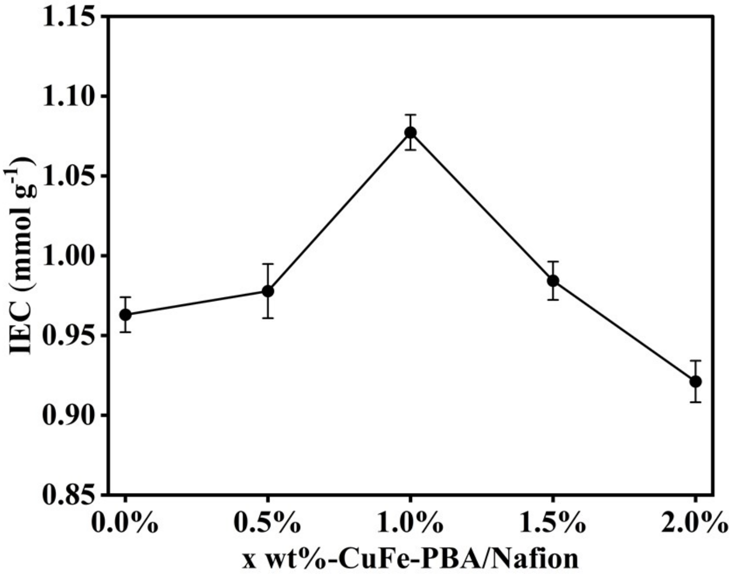

Fig. S7 Proton Exchange Capacity of CuFe-PBA/Nafion-x Composite Membranes.

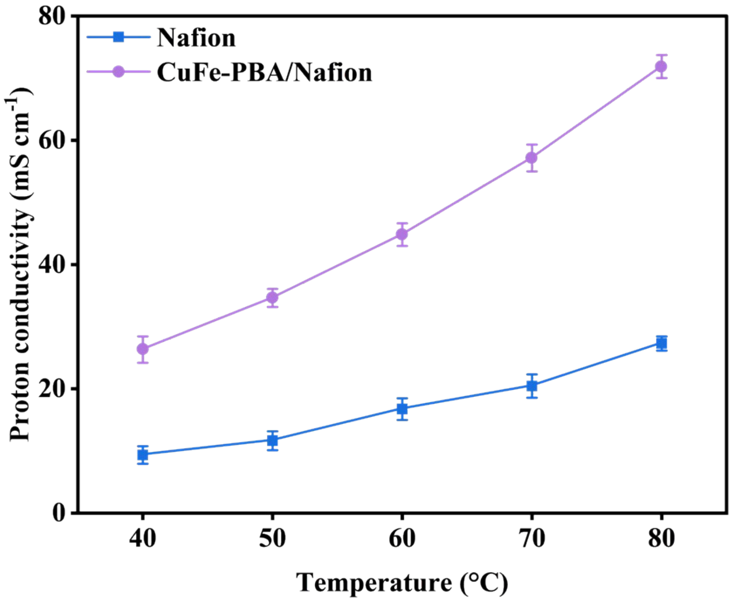

Fig S8 Relationship between proton conductivity and temperature for the pristine Nafion and 1.0 wt%-CuFe-PBA/Nafion composite membranes under 75% relative humidity.

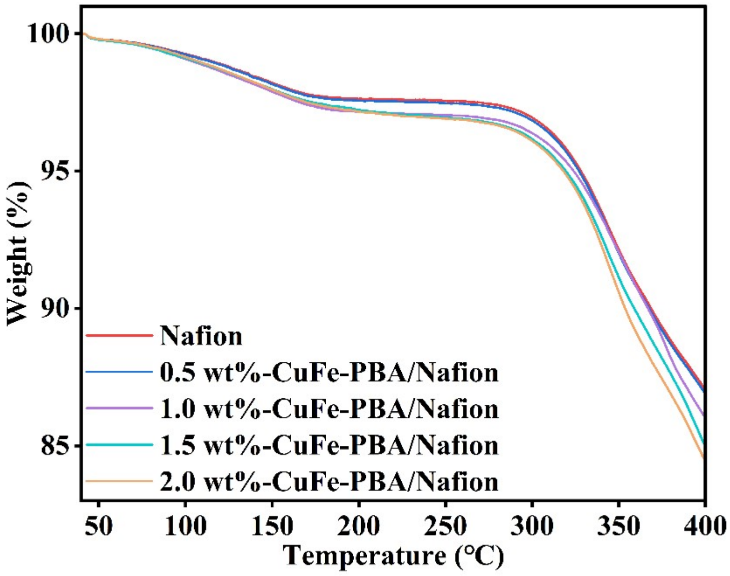

Fig S9 TGA curve of the x wt%-CuFe-PBA/Nafion composite membrane.

Table S1 Comprehensive properties of the *x* wt%-CuFe-PBA/Nafion composite membranes.

Membrane	Tensile strength (MPa)	Elongation at break (%)	Weight loss after Fenton test (%)
Nafion	15.16	$1_27.06$	3.73
0.5 wt%-CuFe-PBA/Nafion	14.8	$1_20.3$	3.67
1.0 wt%-CuFe-PBA/Nafion	14.6	115	3.57
1.5 wt%-CuFe-PBA/Nafion	13.3	107	3.13
$_2$ wt%-CuFe-PBA/Nafion	11.76	96.1	4.08