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Electronic Supporting Information

A novel polyetherimide hydrogel proton exchange membrane

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1. Materials and methods

1.1 Chemicals and materials

Polyetherimide (MI 9g/10min), polyethyleneimine (99%, M.W. 600), N, N-dimethylformamide (concentration >99.9%, purchased from Aladdin), concentrated sulfuric acid (H_2SO_4, concentration >96.8%, purchased from Shanghai Tianhong Chemical Co., LTD.) All the chemicals were used as received without further purification.

1.2 Characterization methods

1.2.1 Fourier transform infrared spectroscopy (FTIR) analyses

The Fourier transform infrared spectroscopy (FT-IR) analysis was carried out with a Nicolet iS50 Fourier transform infrared spectrometer from Thermo Fisher Scientific (China) with a spectral range of 7800-350 cm^{-1}. The samples were dried under a vacuum for 48 h beforehand.

1.2.2 Scanning electron microscopic (SEM) images

Scanning electron microscopic (SEM) images were taken on a Gemini SEM500 high resolution scanning electron microscope from ZEISS (Germany). The samples were horizontally attached to an aluminum support for imaging of the membrane surface. As for cross-sectional imaging, the samples were frozen and fractured with liquid nitrogen. All samples were dried at 50°C overnight.

1.2.3 Brunauer-Emmett-Teller (BET)

The specific surface area and the pore volume were obtained using a Micrometrics Tristar 3000 at 77 K with N_2. The samples were first degassed at 120 °C for 8 h. Their specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method at a relative pressure of $P/P_0=0.99$.

2. Experimental section and discussion

2.1 Preparation of the polyetherimide Gel-membrane

The polyetherimide (2 g) and polyethyleneimine (2 g) were dissolved in N, N-dimethylformamide (DMF, 20 mL) at 65°C to obtain polyetherimide solution and polyethyleneimine solution. The two solutions (1:1) were then mixed in a glass dish (r=3 cm) and Shaked quickly in room temperature. The mixture solution was solidified in 10 s. As shown in Fig. S1, the Gel-membrane formed by cross-linking of polyetherimide and polyethyleneimine via amide bond. However, due to the rigidity of polyetherimide backbone, the Gel-membrane showed limiting flexibility, the DMF Gel-membrane showed cracks because of the losing of DMF (Fig. S1). The other membrane samples with mass ratios of 2:1, 1.5:1 and 1:1.5 were prepared by the same method.

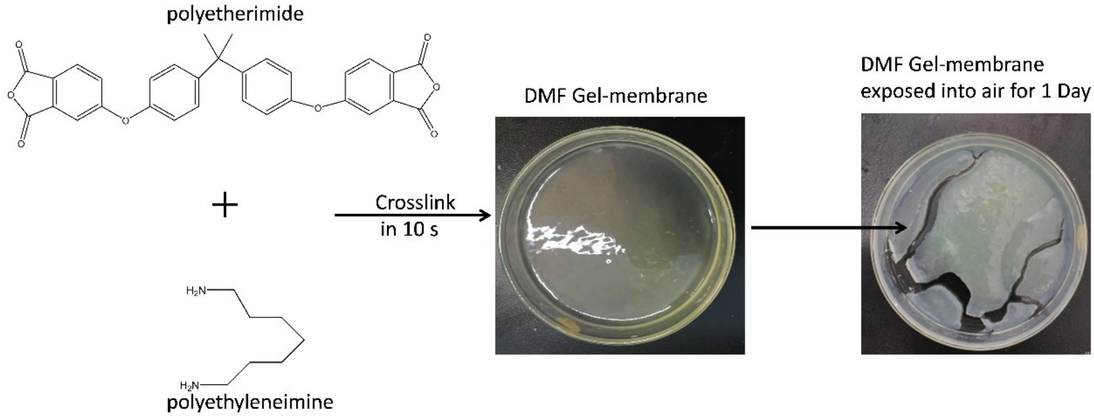

Fig. S1. Schematic diagram of the fabrication process of the novel polyetherimide DMF Gel-membranes.

2.2 Preparation of the polyetherimide hydrogel membrane

The hydrogel membranes were obtained by solvent exchange method. The prepared polyetherimide DMF Gel-membranes were soaked by pure water for 5 times in 48 h for displacing the DMF molecules into H_2O. The obtained hydrogel membranes were shown in Fig.S2. The yellow color of the hydrogel membranes gradually became lighter due to the decrease of the content of the polyetherimide.

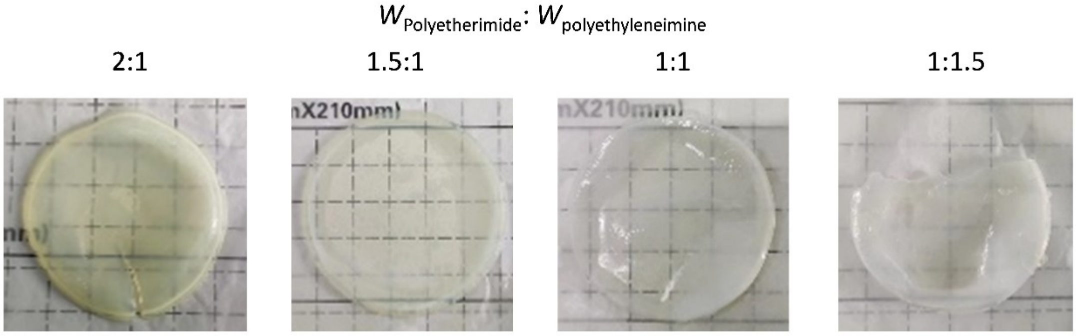

Fig.S2. The photos of the hydrogel membranes with the quality ratio ($W_{\text{Polyetherimide}}$: $W_{\text{polyethyleneimine}}$) which was set to 2:1, 1.5:1, 1:1 and 1:1.5.

The water retention capacity of the obtained hydrogel membranes was then tested. The hydrogel membranes were put in an oven at 100°C (RH=0), the change of area and weight were shown as Fig.S3. The aera was calculated by ImageJ, the weight was tested by quartz crystal microbalance. Fig. S3 indicated that the hydrogel membranes (1:1) exhibited better H_2O retention capacity due to the suitable hydrophily and pore structure.

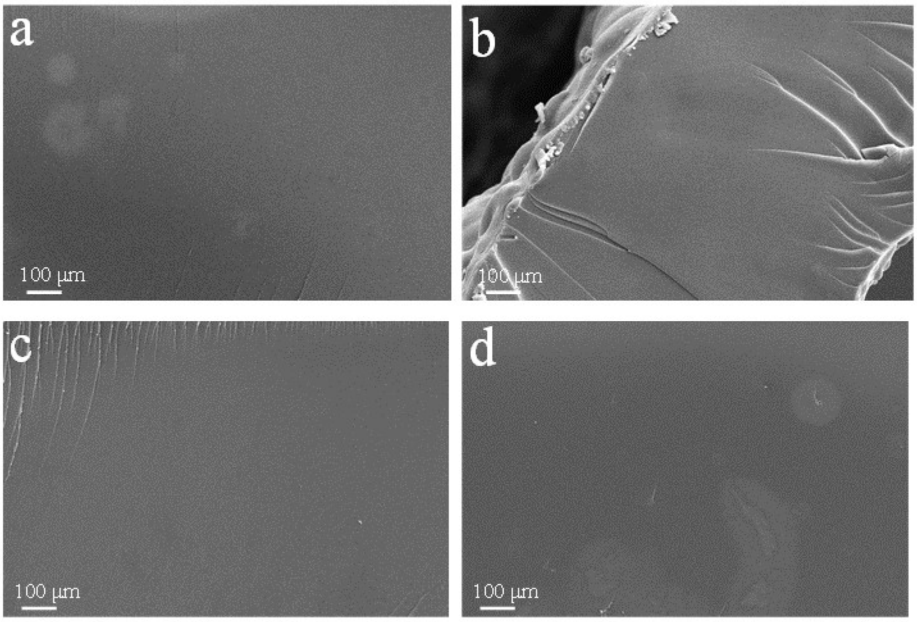

Fig.S3. Cross-section SEM images of the hydrogel membranes obtained after drying, (w polyetherimide: polyvinyl imide = 2:1 (a), 1.5:1 (b), 1:1 (c) and 1:1.5 (d).

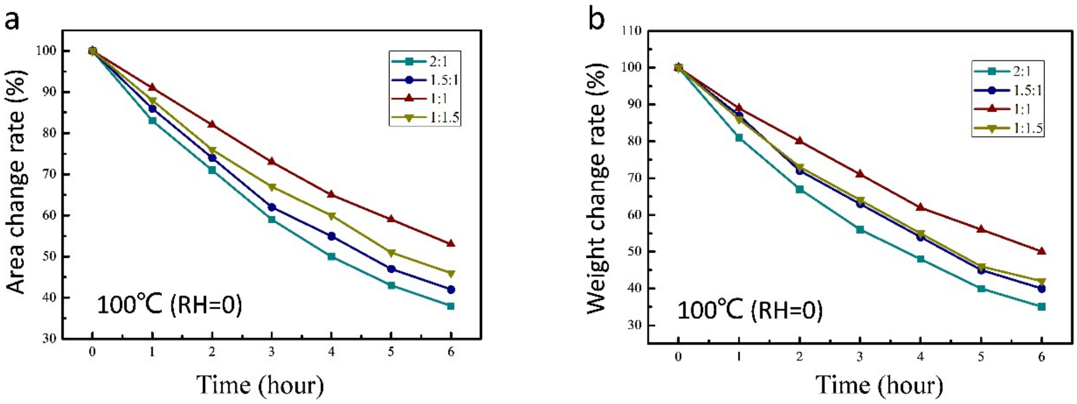

Fig.S4. The water retention capacity of the obtained hydrogel membranes, the change of area (a) and weight (b).

3 Membrane performance

3.1 The proton conductivity of the hydrogel membranes

Before proton conductivity measurement, the hydrogel membrane samples (1cm × 4cm) with different mass ratios were soaked in 0.5mol/L H_2SO_4 solution for 24h, then placed in a four-electrode testing fixture (Fig.S4). The testing fixtures were then put into an oven with a humidification device. The electrical properties of the obtained hydrogel membranes were tested via four-electrode AC impedance method with the electrochemical workstation (CHI760e, Shanghai Chenhua Instrument Co., Ltd., China). The AC impedance frequency for the test was set to 0.1-100KHz. The conductivity σ ($S \cdot cm^{-1}$) was calculated by equation:

$$\sigma = \frac{L}{RA}$$

where R (Ω), A (cm^2) and L (cm) represent the membrane resistance, the crosssectional area of the membranes and the distance between the two electrodes, respectively.

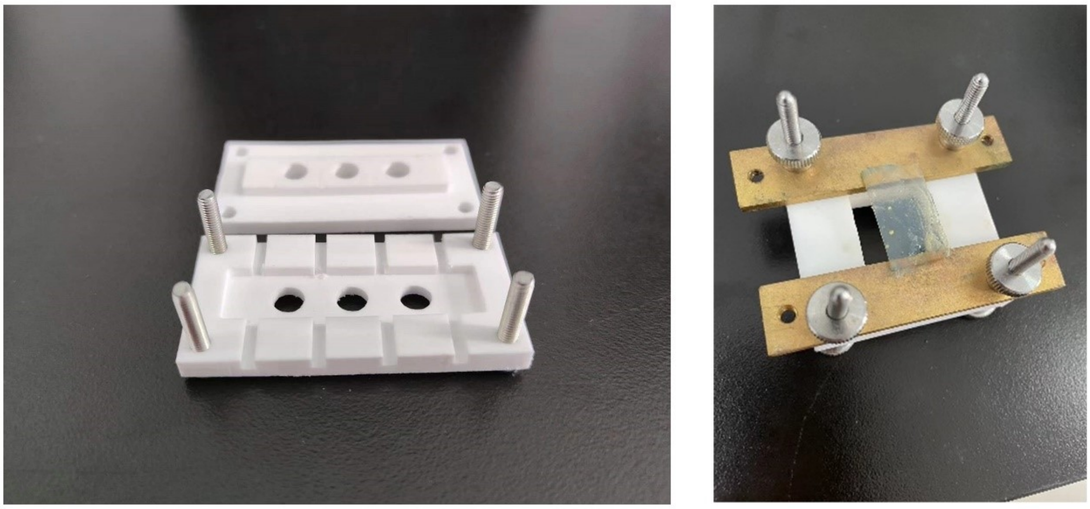

Fig. S5. The photos of four-electrode testing fixture.

3.2 Tensile strength tests

Tensile strength tests were performed at a tensile speed of 10 mm/min, on a YG065 stretching machine (Laizhou Electronic Instrument Co., LTD., China). Each sample (1cm×5cm) was tested 5 times, and an average was taken. The critical strain (ε_c) [36,37] can be calculated using Equation:

$$\varepsilon_c = \frac{1}{4}\left[\frac{3\left(1-\nu_f^2\right)E_s}{\left(1-\nu_s^2\right)E_f}\right]^{2/3}$$

Where E and ν separately express Young's modulus and the Poisson ratio of materials, the subscripts f and s stand for the layer and substrate, respectively.

3.3 Thickness uniformity test

Thickness uniformity testing was conducted using a thickness gauge (with an accuracy of no less than 0.001mm). There were no less than 9 sample testing points, which were evenly distributed, and the distance between the testing points and the edge of the sample should be greater than 5 mm. The uniformity of sample thickness was expressed as the average relative deviation of thickness, and its calculation formula is as follows:

$$d = \sum_{i=1}^{n} \frac{d_i}{n}$$

Where d_i and n separately express the thickness measurement of a membrane at a certain point and the number of measurement data points.

$$S = \frac{(d_{\mathrm{i}} - d)}{d} \times 100\%$$

$$\overline{S} = \sum_{\mathrm{i}}^{\mathrm{n}} \frac{|S_i|}{n}$$

Where S_i and $\overline{S}$ separately express the relative deviation of thickness and the average relative deviation of thickness.

Tale 1 Thickness uniformity of hydrogel membranes

Sample	1:1	1:1.5	1.5:1	2:1
$\overline{S}$	5.69%	3.10%	3.87%	1.79%

3.4 Testing the effect of different thicknesses on tensile strength

Hydrogel membrane(1:1) with different thicknesses were prepared according to Step 2.1. Then, the Tensile strength of hydrogel membrane with different thicknesses were tested(The thicknesses are 1.3, 1.5, 1.7, and 1.9mm, respectively). Fig. S6 indicated that the Stress increased with the increase of the thickness of the hydrogel membrane, however the Elongation decreased.

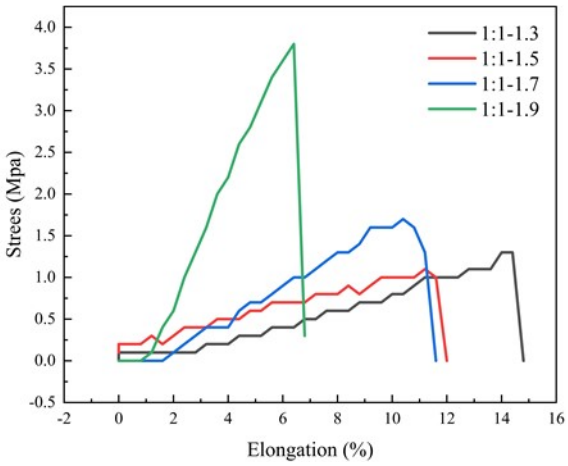

Fig.S6. The tensile testing of the 1:1 hydrogel membrane (The thicknesses are 1.3, 1.5, 1.7, and 1.9mm, respectively).

Tale 2 Proton conductivity of this work in comparison with other proton conducting materials reported

Sample	Conductivity(S/cm)	Conditions	Cost	Ref.
1:1	1.24×10^{-1}	140 °C and 100% RH	\$45/m^2(form Adamas)	This work
Nafion N-117	1.33×10^{-2}	30 °C and 100% RH	\$600-\$1200/m^2(form Dopont)	[1, 2]
Nafion N-901	1.05×10^{-2}	30 °C and 100% RH		
Nafion NR-211	7×10^{-2}	25 °C		
ETFE-SA	1×10^{-2}	25 °C	\$30-\$100/m^2	[3]
SPEEK-Z1	5.5×10^{-2}	120 °C	\$375/m^2(Cost of SPEEK)	[4]
Pall R-1010	3.33×10^{-2}	30 °C and 100% RH	-	[1]

SFPAE-S-70	7.8×10^{-2}	At room temperature	-	[5]

Notes and references

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