

## *Supporting Information*

### **A composite proton exchange membrane with three-dimensionally-reinforced hydrogen bonding network for durable hydrogen fuel cells**

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## **Experimental section**

### **Materials**

All chemicals and solvents were of reagent quality and used without further purification. Perfluorosulfonic acid (PFSA) resin was purchased from Kedi Chemical Technology Co., LTD (China). N-Methylpyrrolidone (NMP) (>99.9%) was purchased from BASF Co. Ltd., Mainland, China. Gore-select was purchased from Alfa Aesar. Tannic acid and trimethylamine hydrochloride (Tris-HCl) were purchased from Shanghai Titan Technology Co. Ltd. Zirconium oxide nanoparticles, tetraethylenepentamine and ferrous chloride tetrahydrate were purchased from Adams Reagent. ePTFE was purchased from Shenzhen Sheng'an Technology Co. Ltd. Isopropanol was purchased from Merck Chemicals.

### **Experimental procedures**

#### **(1) ePTFE membrane hydrophilic treatment (TA@ePTFE)**

Firstly, 500 ml of Tris-HCl buffer was prepared with a solvent mixture of ethanol: water in a volume ratio of 2:1 at a pH of about 8.5. Then 1 g of tannic acid powder was added to the buffer and stirred to dissolve. The ePTFE was then held in place with a stainless steel box and the entire ePTFE membrane was placed into the tannic acid solution. Then 400  $\mu$ L of tetraethylenepentamine was added dropwise to the buffer solution. The mixed solution was stirred continuously for 12 hours in a light-free environment. The catechols in tannic acid and the amine groups in tetraethylenepentamine can polymerize on the surface of ePTFE fibres by Michael

addition reaction, thus making the surface of ePTFE hydrophilic. The modified ePTFE is denoted as TA-ePTFE. After the modification is completed, the TA-ePTFE is dried in an oven at 40 °C for 12h.

## **(2) Preparation of TA@ZrO<sub>2</sub>**

TA@ZrO<sub>2</sub> was synthesized by a modified mussel-inspired method [224, 225]. First, 100 mg of ZrO<sub>2</sub> nanoparticles was dispersed and stirred in Tris-HCl buffer (100 mL, pH 8.5). Then, tannic acid (50 mg) and tetraethylenepentamine (20 μL) were added to the above solution and the mixture was stirred for 8 h under dark conditions. Finally, the dried solid product was obtained by centrifugation, washing and vacuum drying steps and designated as TA@ZrO<sub>2</sub>.

## **(3) Preparation of TA@ZrO<sub>2</sub>/ePTFE RCM and ePTFE/PFSA**

The PFSA resin was first dissolved with NMP to obtain a homogeneous solution. Then the PFSA/NMP solution was diluted to 3% mass fraction with ethanol. Then a certain amount of TA@ZrO<sub>2</sub> nanoparticles was added to the PFSA solution, and TA@ZrO<sub>2</sub> was controlled to account for 3 wt.% of the solute solid content. The prepared membranes (pristine ePTFE or TA-ePTFE membrane) were gently placed on the glass substrate and fixed with adhesive tape, and the squeegee was coated at a constant speed of 3 mm s<sup>-1</sup>. The pristine PFSA or PFSA solution with 3 wt.% TA@ZrO<sub>2</sub> was uniformly squeegeed onto the ePTFE membrane. The membranes attached to the glass substrate were dried in an oven at 80 °C for 12 h. Then, the membranes were carefully separated from the glass substrate by vacuum heat treatment at 140 °C for 120

min. The membranes obtained were denoted as ePTFE/PFSA and TA@ZrO<sub>2</sub>/ePTFE RCM. The electrolyte membrane thickness is 12 μm.

#### **(4) Post-processing of reinforced composite membranes**

All membranes were subjected to the following steps after preparation. (i) heat with 3% H<sub>2</sub>O<sub>2</sub> solution at 80 °C for 1 h to remove organic impurities, then rinsing with deionized water. (ii) Activate with 1 M aqueous H<sub>2</sub>SO<sub>4</sub> solution, heated at 80 °C for 1 h, then rinse with deionized water. (iii) Remove excess H<sub>2</sub>SO<sub>4</sub> by heating with deionized water at 80 °C. Finally, dry the membrane with dust-free paper and store it for use.

### **Characterization**

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out on SEM, Nova NanoSEM 450 Fei, USA, and JEM-2010 systems at 220 Kv, respectively. Fourier-transform infrared spectroscopy (FTIR) was tested with Nicolet iS10 (Thermo Fisher Scientific, USA). An XRD spectrometer (Bruker D8, Germany) was employed for X-ray diffraction (XRD) analysis with Cu (K $\alpha$ =1.54178Å) radiation source operated at 40 mA and 40 kV over the 2 $\theta$  range of 10°-80°. Thermogravimetric analysis (TG) was performed using a thermogravimetric analyser (NETZSCH STA 449F3, Germany) under N<sub>2</sub> atmosphere at a scan rate of 10 °C min<sup>-1</sup>. The surface hydrophilic and hydrophobic properties of the PEM were obtained by analysis using a Thetalite contact angle meter with deionized water as the

liquid. During the test, the measured contact angle values were read after the liquid was dropped onto the membrane surface for 5s.

## **Electrochemical characterization**

### **Swelling rate test**

The dimensional stability of the proton exchange membrane was responded by the swelling rate data. The samples were cut into rectangles of 2 cm × 3 cm and dried at 90 °C for 24 h. The length ( $L_{dry}$ ), width ( $W_{dry}$ ), and thickness ( $T_{dry}$ ) of the dry membranes were measured with a graduated scale, and the samples to be tested were then stored in deionized water, and after complete immersion for 24 h, the wet membranes were again tested for the length ( $L_{wet}$ ), width ( $W_{wet}$ ), and thickness ( $T_{wet}$ ) of the water-absorbed membranes.

The swelling rate in the lengthwise direction (LSR) of the PEM was calculated with Equation 1:

$$LSR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \quad (1)$$

The swelling rate in the thickness direction (TSR) of the PEM was calculated with Equation 2:

$$TSR = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100\% \quad (2)$$

### **Chemical stability testing**

The oxidation resistance of the prepared composite membranes was tested by the Fenton method. Fresh composite membranes were dried, weighed and then immersed in 50 mL of Fenton solution (5 wt.%  $H_2O_2$ , 5 ppm  $Fe^{2+}$ ) at 80 °C. The membranes were then treated with Fenton solution (5 wt.%  $H_2O_2$ , 5 ppm  $Fe^{2+}$ ). The Fenton solution was renewed every 24 h to maintain the concentration of  $H_2O_2$  and the degraded membranes were rinsed with deionized water, dried, and weighed before the next round of

degradation tests.

### **Single cell performance test**

The discharge performance of the PEM was recorded and analyzed using the Arbin fuel cell system in the USA. The polarization curves and power density curves of the membrane electrodes were tested under two conditions, 80 °C@100% RH, and 80 °C@50% RH, respectively. The anode was hydrogen at a controlled flow rate of 150 mL/min and the cathode was oxygen at a controlled flow rate of 200 mL/min, and the back pressure of the gas was 0.7 MPa. The relative humidity of the cathode gas was controlled by setting different gas temperatures and dew point humidification temperatures. Johnson Matthey Company 40 wt.% Pt/C catalyst was used, and the anode Pt catalyst content was approximately 0.2 mg cm<sup>-2</sup>. The cathode catalyst content was approximately 0.3 mg cm<sup>-2</sup>. The MEAs were obtained by spraying directly on both sides of the membrane with a pneumatic spray gun. Toray 060 carbon paper with a microporous layer was used as the gas diffusion layer. The PEM with catalyst and the carbon paper formed a GDL-CCM membrane electrode with an effective area of 4 cm<sup>2</sup> without a hot-pressing process. All test data were activated at a constant voltage (0.4 V) for 6 h before formal tests.

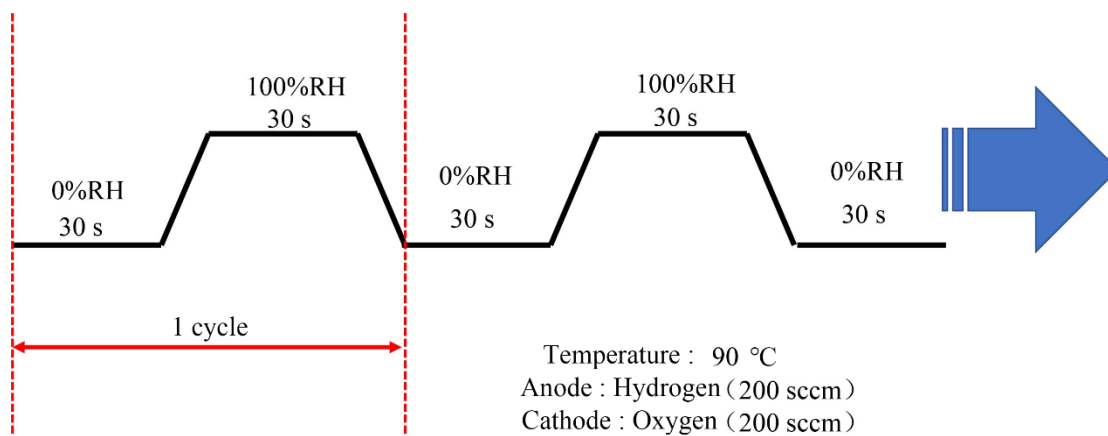
### **Hydrogen permeation current density test**

The hydrogen permeation current density of MEA was investigated by linear sweep voltammetry (LSV) using the CHI760E electrochemical workstation. An interfering voltage was applied at a dynamic sweep rate of 2 mV s<sup>-1</sup> over a voltage range

of 0 to 0.8 V. The anode was supplied with H<sub>2</sub> (100% RH) at a flow rate of 200 sccm and the cathode was supplied with N<sub>2</sub> (100% RH) at a flow rate of 200 sccm. The H<sub>2</sub> permeation current density was determined from the limiting current density at a higher potential (0.4 V). Cells were kept open-circuited for more than 4 hours before formal testing.

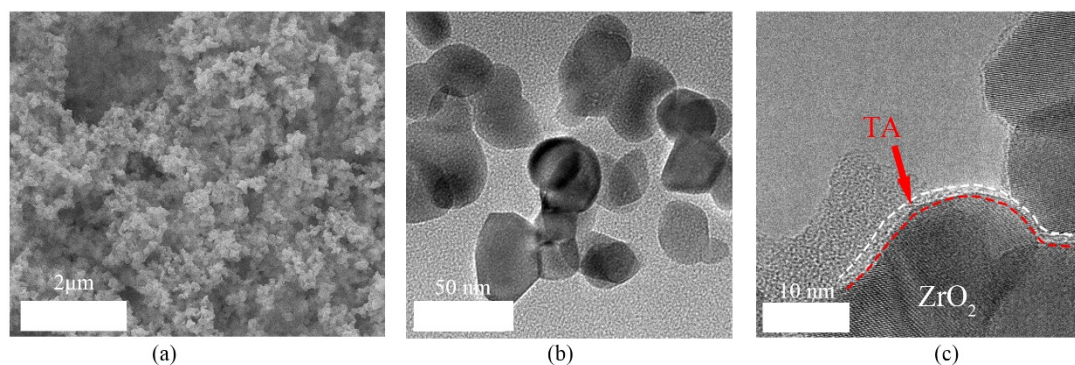
### MEA's dry/wet accelerated cycle test

After an initial evaluation of cell performance for a given fuel cell, a humidity cycling test designed to incorporate chemical/mechanical durability was conducted to examine the effect of a three-dimensional interfacial enhancement treatment on cell performance under repeated dry/wet changes. In this experiment, un-humidified hydrogen was applied at a flow rate of 200 sccm and oxygen was vented every 30 s at a rate of 200 sccm; in addition, fully humidified hydrogen was applied at a rate of 200 sccm and oxygen was vented every 30 s at a rate of 200 sccm, with the specific test procedure shown in Fig. S2. The cell temperature was set at 90°C. During these repeated cycles the obtained curves for all humidity cycles and post-cycle hydrogen permeation curves were obtained.

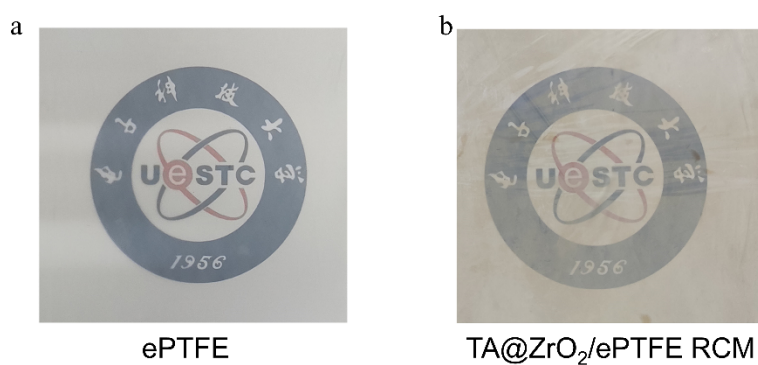


**Figure S1.** Combined chemical/mechanical durability accelerated test programme (modified DOE test

protocol).



**Figure S2.** Morphology of TA@ZrO<sub>2</sub> nanoparticles. **a**, SEM. **b**, TEM. **c**, HRTEM.



**Figure S3.** The digital photograph of the **a**, original ePTFE and **b**, TA@ZrO<sub>2</sub>/ePTFE RCM membrane.

**Table S1.** Basic properties of different membranes

Sample	WU (%)	LSR (%)	TSR (%)	EW (g mol <sup>-1</sup> )
ePTFE/PFSA	11.4	4.1	11.7	1240
TA@ZrO <sub>2</sub> /ePTFE RCM	15.8	1.3	7.1	1300
Gore-Select	10.8	3.3	11.1	1260

Note: Water uptake (WU); Lengthwise swelling rate (LSR); Thickness-direction swelling rate (TSR); Equivalent weight (EW).