

*Electronic Supplementary Information*

## High quality pristine perfluorosulfonated ionomer membranes prepared from perfluorinated sulfonyl fluoride solution

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#### Experimental Section

##### Perfluorinated sulfonyl fluoride (PFSF) solution and PFSI membranes preparation

25 Dissolution of PFSF has been achieved by swelling PFSF resin in HFPT (2 wt%) and heating for 2 h  
at 250 °C under pressure. The filtered solution was cast on glass plates and dried under ambient  
conditions. The resulting membranes were further dried in vacuum oven at 80 or 160 °C for 2 h to  
remove the residual solvent. Upon cooling in oven, the membranes were peeled off in an alkali  
solution heated to 80 °C.

30 The obtained membranes as well as melting extruded PFSF membranes were transferred to 8 M

NaOH solution and refluxed at 80 °C for 48 h to convert  $\text{SO}_2\text{F}$  groups to  $\text{SO}_3\text{Na}$  units. After treatment, the membranes were repeatedly immersed (three times) in a fresh 5 M  $\text{HNO}_3$  for 1 h to obtain the samples of P80, P160 and MEM.

5 wt% PFSI in DMF was prepared in an autoclave at 230 °C for 4 h. Then, the filtered solution was subsequently condensed to 10 wt% and cast on a glass plate. After being dried at 80 °C for 1 h, the membrane was heated to 160 °C and annealed for 2 h, meanwhile to remove the residual solvent. Finally, the membrane was peeled off from the glass plate and named as RCM.

All membranes were purified according to the standard procedure before measurements. The resin with an IEC value of 1.02 meq/g used above was synthesized in the same batch in Dongyue Shenzhou New Materials Company Ltd., China.

### Particle size distribution of PFSF solutions

PFSF solution prepared in autoclave was filtered through microporous filtering films with the pore size of 5  $\mu\text{m}$  three times. The solution concentration was identified by evaporating the solvent from a small quantity of solution under vacuum at 120 °C overnight. Then, the solutions were diluted to 0.1 wt%. Particle size distribution was determined by a Particle Size and Zeta Potential Analyzer (ZS90, Malvern Instruments Ltd, UK). As shown in Fig. S1, PFSF molecules were aggregated in hexafluoropropene trimer (HFPT) and the particle size is increased with decreasing IEC value. Double peaks were observed in the PFSF solution with an ion exchange capacity (IEC) value of 0.87 meq/g.

### Purification process

The membranes were treated according to the standard procedure described in reference<sup>1</sup>. Briefly, the membranes were boiled in 5%  $\text{H}_2\text{O}_2$  aqueous solution for 1 h and washed with boiling deionized water for 30 min. Then they were boiled in 1 M  $\text{H}_2\text{SO}_4$  for 1 h before washing with deionized water for 30 min. Washing with deionized water was repeated several times to remove any trace of acids, as checked by pH paper. Finally, all membranes were kept in deionized water prior to measurement.

### DMA measurements

The hydrolyzed as well as unhydrolyzed PFSF melting extruded membranes were measured through dynamic mechanical analysis (DMA) on a DMA 7e instrument (Perkin Elmer, USA). Membranes were cut into small pieces (around 20 mm  $\times$  6mm) and analyzed in the tensile mode under nitrogen at a frequency of 1 Hz and a heating rate of 5 °C/min. The result is shown in Fig. S2. Clearly, the glass transition temperatures ( $T_g$ ) of PFSF and PFSI are 19 and 127 °C, respectively.

## TGA measurements

TGA measurements were carried out on a TGA Q50 V6.5 Build 196 instrument (TA Instruments, USA). About 10 mg dry samples were heated from room temperature to 700 °C under nitrogen at a heating rate of 10 °C/min.

## 5 Measurements of PFSI membrane properties

**Proton conductivity measurement:** Proton conductivity of the membranes was measured with AC impedance method by using an Autolab PGSTA302 electrochemical test system at 15 °C and 100% R.H. The membrane was clamped on a self made cell equipped with two parallelized platinum electrodes<sup>2</sup>. Proton conductivity ( $\sigma$ ) was calculated from Equation 1:

$$\sigma = \frac{L}{RA} \quad (1)$$

where  $L$  is the distance between the electrodes,  $A$  is the cross sectional area of the membrane, and  $R$  is the resistance of the membrane.

**Methanol crossover measurement:** The methanol crossover of each membrane was investigated at room temperature using a home-made diffusion cell, which is consisted of two identical compartments<sup>3</sup>. The testing membrane was clamped between two compartments filled with 2 M methanol solution and deionized water, respectively. Both compartments were stirred during the permeation experiment and the concentration of the permeated methanol versus time was measured by gas chromatography. The crossover was calculated from the slope of the linear plot of methanol concentration versus permeation time.

**Solubility in solvent measurement:** Membranes were dried in vacuum oven at 80 °C for 24 h, a quantity of the dry membranes ( $W_1$ ) were immersed into a mixed solvent composed of 50:50 (v/v) water/ethanol and dissolved under ultrasonication for 2 h. Then, the remaining membranes were dried again in vacuum oven at 80 °C for 24 h and weighted as  $W_2$ , the solubility were calculated as Equation

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$$\text{Solubility} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (2)$$

**SAXS analysis:** All swollen membranes were sealed by Scotch<sup>®</sup> Magic<sup>™</sup> Tape in case water losses in experimental, and the Scotch<sup>®</sup> Magic<sup>™</sup> Tape is transparent in X-ray. The SAXS measurements carried out in SAXSess mc2 instrument (Anton Paar, Austria) with a Cu K $\alpha$  X-ray source (40 kV, 35 mA).

**XRD analysis:** The membranes were dried in vacuum oven at 80 °C for 24 h. The dried samples were tested in Shanghai synchrotron radiation facility and the X-ray wavelength is 0.12398 nm. The relative crystallinity ( $X_c$ ) was calculated using Equation 3 as described by Hensley et al.<sup>4</sup>:

$$X_c = \frac{\int_0^\infty I_{cr}(s)s^2 ds}{\int_0^\infty [I_{cr}(s) + I_{am}(s)]s^2 ds} \times 100 \quad (3)$$

where  $I_{cr}$  is the relative intensity of the deconvoluted crystalline peak centered at 14.1°,  $I_{am}$  is the relative intensity of the deconvoluted amorphous peaks centred at 12.7° and 31.6°, and  $s$  is the magnitude of the reciprocal-lattice vector determined by Equation 4:

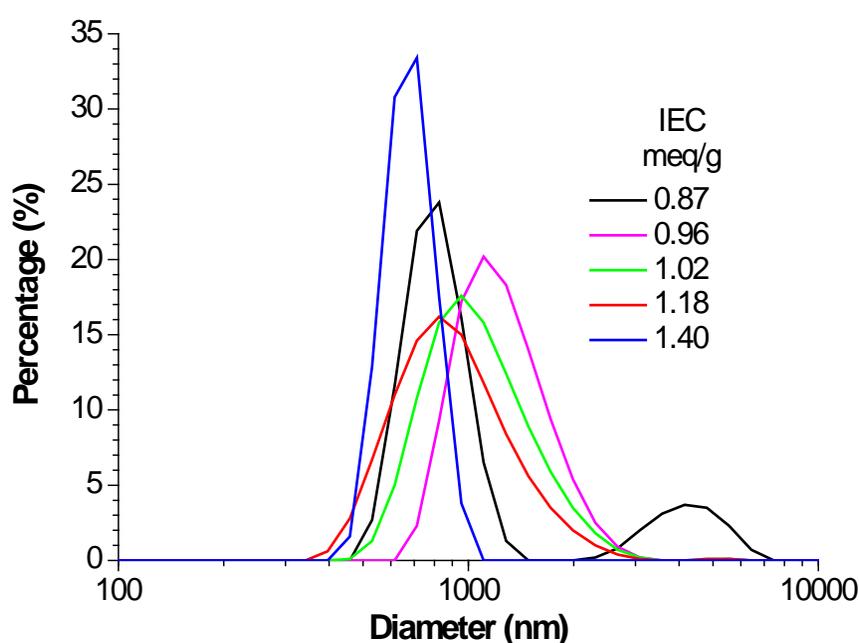
$$s = \frac{2 \sin(\theta)}{\lambda} \quad (4)$$

where  $2\theta$  is the diffraction angle (°), and  $\lambda$  is the X-ray wavelength (0.12398 nm).

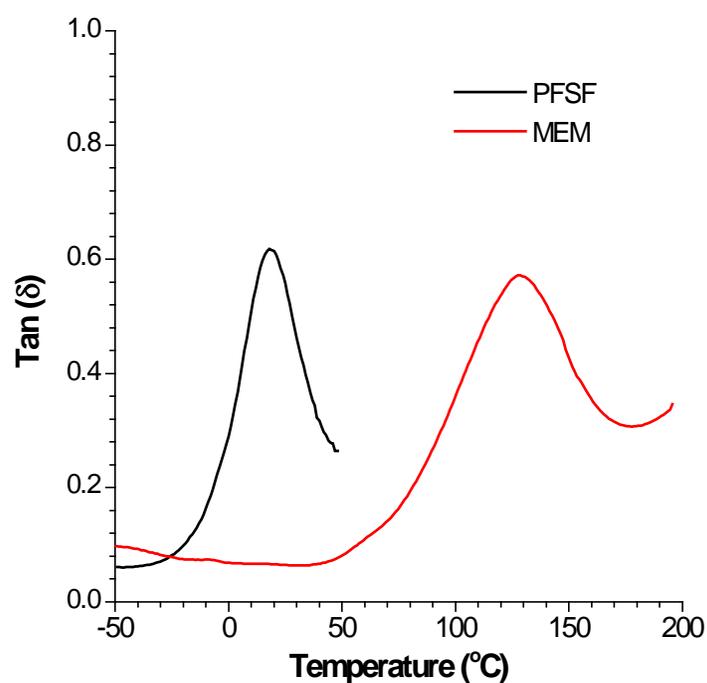
All data obtained by the above mentioned method were listed in Table S1.

### Fenton reaction experiment

Fenton experiments were conducted using the reagents of 3 wt% H<sub>2</sub>O<sub>2</sub> and 3 ppm Fe(II). Four pieces of sample marked with slight difference in shape were placed in a 500 ml beaker, then 300 ml of Fenton reagent was added and the beaker was placed in a 30 °C water bath. In case the sample was floated on the solution surface due to the gas flow originated from the reaction, magnetic stirring was used to form a whirlpool to ensure all membranes immersed into the reagent. The reagent was refreshed every 10 h.



**Fig. S1** Size distribution of PFSA aggregates in 1 wt% HFPT solutions.



**Fig. S2** DMA profiles of PFSF and PFSI (MEM) membranes measured under nitrogen at a frequency of 1 Hz and a heating rate of 5 °C/min.

**Table S1.** Properties of membranes prepared by different methods

Membranes	P160	P80	RCM	MEM
Thickness of dry membrane (μm)	24	23	25	95
Volume Gain % (100ΔV)	62.7	65.9	76.8	68.5
Mass Gain % (100Δm)	31.3	33.0	38.9	34.3
Proton Conductivity (mS/cm)	97.2	87.3	82.4	64.5
Methanol Permeability 10 <sup>-6</sup> (cm <sup>2</sup> /s)	0.509	0.536	0.845	1.560
Solubility in Solvent (%)	4.30	4.87	9.01	3.27
Relative crystallinity (%)	8.62	7.87	5.97	7.36
FWHM (°)	1.062	1.098	1.119	1.200
Crystalline size (nm)	6.00	5.80	5.69	5.31

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