Electronic Supplementary information (ESI) for

Highly sulfonated co-polyimides containing hydrophobic cross-linked network as proton exchange membranes

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A. Supplementary Method

1. Materials

4,4'-Diamindodiphenylether-2,2'-disulfonic acid (ODADS) was synthesized according to synthesis routines reported by Okamoto et al.[1] 2, 3, 4, 5, 6-Pentafluorostyrene, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and 1,4,5,8-naphthalenetetracarboxylicdianhydride (NTDA) was purchased from TCI chemical company. Calcium hydride and cesium fluoride were purchased from Energy Chemical Co., Ltd. (China). Triethylamine (TEA), m-cresol, N, N-dimethylacetaminde (DMAc), dimethyl sulfoxide (DMSO) and benzoic acid were purchased from Aladdin Reagents Co., Ltd. (China). Fuming sulfuric acid (SO_3 30%), hydrochloric acid and acetone were purchased from Tianjin Chemical Reagent (China) and were used as received.

2. Synthesis of diamine monomer

2,2-Bis(3-amino-4-(2,3,5,6-tetrafluoro-4-vinylphenoxy)phenyl)hexafluoropropane (6FATFVP)

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (0.7325 g, 2 mmol), 2, 3, 4, 5, 6-pentafluorostyrene (0.7848 g, 4 mmol), calcium hydride (0.1712 g, 4 mmol), and cesium fluoride (0.0618 g, 0.4 mmol) were added into a 25 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a water condenser (Scheme 1). Then, DMAc (10 mL) was added into the flask under the nitrogen atmosphere. The mixture was heated to 80 ^oC with stirring under nitrogen in the dark for 18 h. After cooled to room temperature, it was poured into 150 mL deionized water, washed with deionized water, extracted with ether, dried with anhydrous $MgSO_4$, and then filtrated. The solvent was evaporated under vacuum, and the residue was then purified by column chromatography (petroleum ether/ethyl acetate) to afford the pure products. Yield: 79%. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 5.48 (s, 4H, NH_2), 5.81-5.85 (d, J=12 Hz, 2 H), 6.04-6.10 (d, J=18

Hz, 2 H), 6.39-6.42 (d, J=9 Hz, 2 H), 6.67-6.73 (m, 2 H), 6.77-6.80 (d, J=9 Hz, 2 H), 6.84 (s, 2 H). Mass spectrum: m/z 713.2.

3. Synthesis of sulfonated co-polyimides

A typical polycondensation procedure, illustrated by preparation of the SPI80-6FATFVP20 (where 20 and 80 is the molar percentage of monomer 6FATFVP and ODADS in the total diamine monomers, respectively), can be described as follows (Scheme 2). To a 50 mL completely dried three-necked round-bottomed flask, 0.5766 g (1.6 mmol) of ODADS, 10 mL of m-cresol and 0.38 g (3.8 mmol) of triethylamine were added successively under nitrogen flow with stirring. After ODADS was completely dissolved, 0.2856 g (0.4 mmol) of 6FATFVP, 0.5364 g (2 mmol) of NTDA and 0.34 g (2.8 mmol) of benzoic acid were added. The mixture was stirred at room temperature for 30 minutes, and then heated at 80 ^{o}C for 4 h and 180 ^{o}C for 20 h. After cooling to 100 ^{o}C, an additional 15 mL of m-cresol was added to dilute the viscous solution. And then the solution was poured into 300 mL of acetone. The precipitate was collected by filtration, and extracted with acetone in a Soxhletextractor for 48 h. The resulting yellow copolymer was dried in vacuum at 120 ^{o}C for 48 h.

4. Preparation of membranes

The polymer membranes were prepared by solution casting from DMSO. A solution of dried sulfonated copolyimide (in the triethylammonium salt form) in DMSO with a concentration of ~8 wt% was filtered and then cast onto a clean glass plate, and dried at 80 ^{o}C for 10 h and under vacuum at 120 ^{o}C for 24 h. The cross-linked membranes were obtained by treating for 2 h in vacuum oven which was pre-heated to 260 ^{o}C, while the uncross-linked membrane was not thermal treated. After cooling down to room temperature, the membranes were soaked in deionized water and then peeled off. The membranes, in triethylammonium sulfonated salt form, were completely converted to the corresponding sulfonic acid-form membranes by immersing in 1 M HCl at room temperature for 24 h. The membranes were thoroughly washed with deionized water and then dried in vacuum at 120 ^{o}C for 24 h.

5. Measurements

^{1}H NMR spectra of the copolymers were measured on a Bruker AVANCE NMR spectrometer (^{1}H, 300 MHz) using DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal reference. The viscosities of the copolymers were determined by an Ubbelohde viscometer in a thermo static container with a polymer concentration of 0.5 g dL^{-1} in DMSO at 25 ^{o}C.

Ion exchange capacity (IEC)

The IEC values of the membranes were determined by acid–base titration. The dried membrane samples in the acid form were weighed and then immersed in 2.0 M NaCl solution for 48 h to replace the protons of sulfonic acid groups with sodium ions. The solution was titrated by 0.01 M NaOH solution with phenolphthalein as an indicator. The IEC (meq. g^{-1}) values were calculated from the amount of NaOH consumed in the titration and the weights of the dried membrane samples. The volumetric IEC (IEC_v) values were calculated based on water uptake measurements according to the following equation:

$$IEC_v = \frac{IEC}{\frac{1}{\rho_p} + \frac{0.01WU}{\rho_w}}$$

where the IEC is determined by acid-base titration, WU (%) is the water uptake of the membranes, ρ_p (g cm^{-3}) and ρ_w (g cm^{-3}) is the density of polymers and water, respectively.

Water uptake (WU) and swelling ratio measurements

Water uptake and dimensional change were obtained by measuring the weight, length of membranes in the acid form. Before the initial measurements, the membranes were dried in vacuum at 120 ^{o}C for 24 h. Then the membranes were immersed in deionized water to reach equilibrium at the desired temperature. Before weight and length measurements of hydrated membranes, the water on surfaces of membrane was removed. The water uptake (WU) content (%) was calculated by

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where W_{dry} and W_{wet} are the weights of dried and wet membranes, respectively. The water volume fraction (X_v) was the volumetric water uptake according to reference:[2]

$$X_v = \frac{0.01WU}{0.01WU + \frac{\rho_w}{\rho_p}}$$

The swelling ratio was calculated from the change of film length and volume by:

$$Swelling\ ratio = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

$$Volume\ swelling\ ratio = \frac{L_{wet} \times W_{wet} \times T_{wet} - L_{dry} \times W_{dry} \times T_{dry}}{L_{dry} \times W_{dry} \times T_{dry}} \times 100\%$$

The volume swelling ratio is the percentage of volume changes of the membranes in fully hydrated state under different temperature. Where L_{wet}, L_{dry}, W_{wet}, W_{dry}, T_{wet}, T_{dry}, are the lengths, widths and thickness of the wet and dry membranes, respectively.

Proton conductivity

Proton conductivity of fully hydrated membranes (4 cm×1 cm) was measured by a four-electrode AC impedance method from 0.1 Hz to 100 kHz with 10 mV AC perturbation and 0.0V DC rest voltage using a Princeton Applied Research Model 273A potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ) under a temperature in the range of 20-100 °C. The measurements were carried out with the cells immersed in the constant-temperature water. The humidity dependence of the proton conductivity was investigated in water vapor with different RHs at 80°C. Before measurement, the dry membranes were hydrated in different RHs for 24 h in a closed system. The proton conductivity (σ) was calculated from the following equation:

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

where L (cm) is the distance between the counter electrodes and the working electrode, R (Ω) is the resistance of the membrane and A (cm^2) is the membrane area. The activation energy (E_a) of conductivity was calculated by fitting the Arrhenius equation:

$$\sigma = \sigma^0 exp\left(-\frac{E_a}{RT}\right)$$

where R is the gas constant. The effective proton mobility μ ($cm^2\ V^{-1}\ s^{-1}$) was determined as follows:

$$\mu = \frac{\sigma}{Fc(H^+)}$$

where F is the Faraday constant.

Methanol permeability

The methanol permeability of membrane was determined using a diffusion cell consisting of two compartments, each with a capacity of approximately 150 mL, separated by a membrane. Prior to the test, the membranes were equilibrated in deionized water for at least 24 h. The membrane was placed between two compartments. Then one compartment was filled with deionized water and the other filled with a 10 M methanol solution. The solutions in two compartments were stirred continuously during the permeability measurement. Methanol permeated across the membrane by the concentration difference between the two compartments. The concentration of the methanol in the water reservoir was measured by a SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A\ DK}{V_B\ L} C_A(t - t_0)$$

where A (cm^2) is the effective area, L (cm) is the thickness of membrane, V_B (mL) is the volume of the permeated reservoirs. C_A and C_B (mol L^{-1}) are the methanol concentration in the feed and in the permeate, respectively. t and t_0 (s) represent time and the time lag, respectively. The DK (cm^2 s^{-1}) value is the methanol permeability.

Thermal stability

The thermal gravimetric analyses (TGA) of the membranes were performed by a Perkin-Elmer TGA-1 thermo-gravimetric analyzer. Before test, all the membranes were dried and kept in the TGA furnace at 120 °C under nitrogen atmosphere for 30 min to remove water. The samples were evaluated in the range of 100-800 °C at a heating rate of 10 °C min^{-1} under nitrogen.

Oxidative stability

A small piece of the membrane sample was immersed in Fenton's reagent (3 wt% H_2O_2, 2 ppm Fe^{2+}) at 80 °C. The oxidative stability was evaluated by the dissolution time of the membranes and the retained weight of membranes after treating in Fenton's reagent for 1h.

Hydrolytic stability

The hydrolytic stability was investigated by measuring the elapsed time. The time that the membranes dissolved completely in water at 80 °C was considered as the elapsed time. The longer the elapsed time was, the better hydrolytic stability membrane had.

Mechanical property

The tensile properties of dry and wet membranes were measured at room temperature on SHIMADIU AG-I 1KN at a strain rate of 2 mm min^{-1}. The size of samples was 20 mm × 4 mm.

Morphology

Morphological information was gathered from Small-angle X-ray scattering (SAXS) measurements.

The SAXS were measured on membranes where the acidic protons were ion-exchanged for Pb^{2+} using a 1 wt% aqueous solution of $Pb(OAc)_2$. The scattering experiments were performed on a SAXS system with sealed tube X-ray generator (SAXSess mc^2). Hydrated membranes were analyzed in a solid sample holder at 25 °C. The scattering vector q (nm^{-1}) was calculated according to following equation:

$$q = \frac{4\pi \sin\theta}{\lambda}$$

where the wavelength λ is 0.1542 nm and θ is the scattering angle. The characteristic separation length d(nm), i.e. the Bragg spacing, was calculated from following equation:

$$d = \frac{2\pi}{q}$$

B. Supplementary Figures

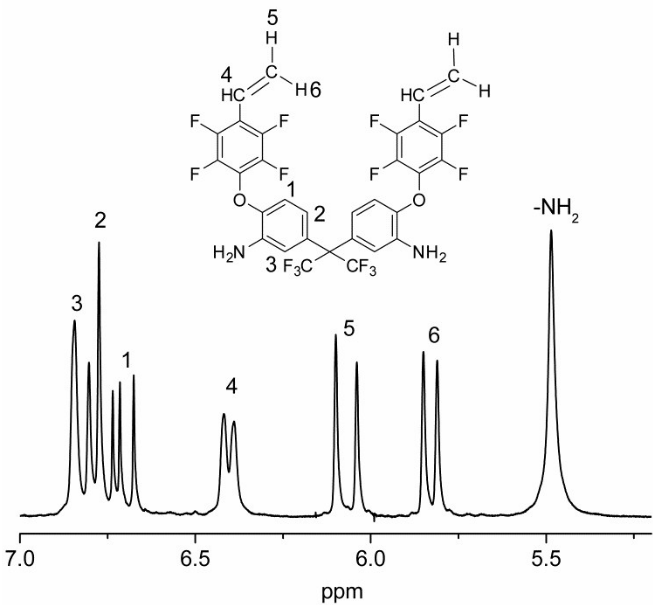

Fig. S1 ^{1}H NMR spectra of 6FATFVP.

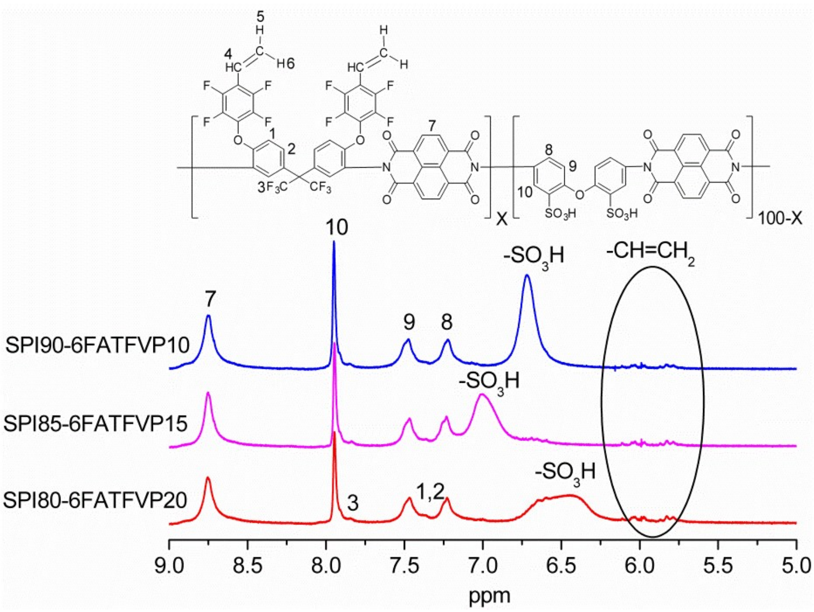

Fig. S2 ^{1}H NMR spectra of SPI-6FATFVPs.

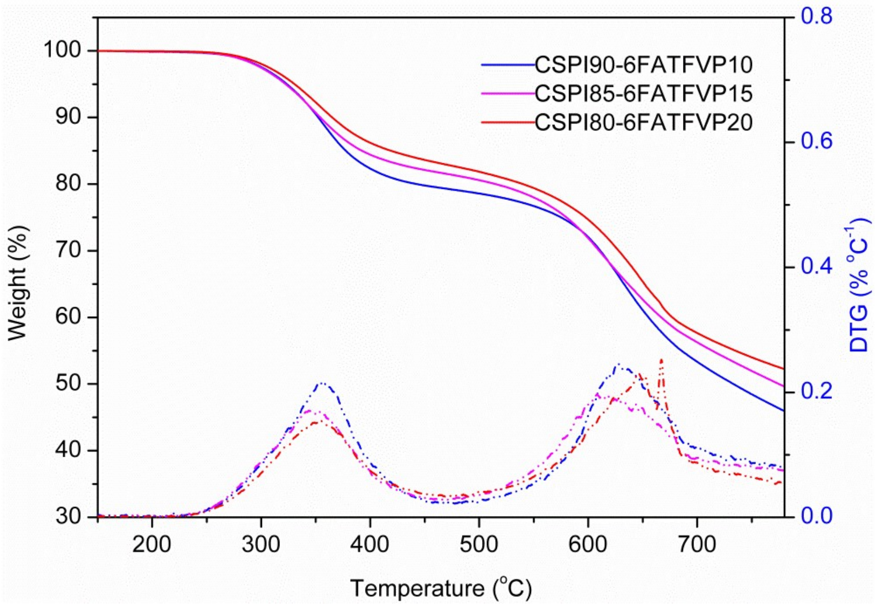

Fig. S3 TGA curves of CSPI-6FATFVPs.

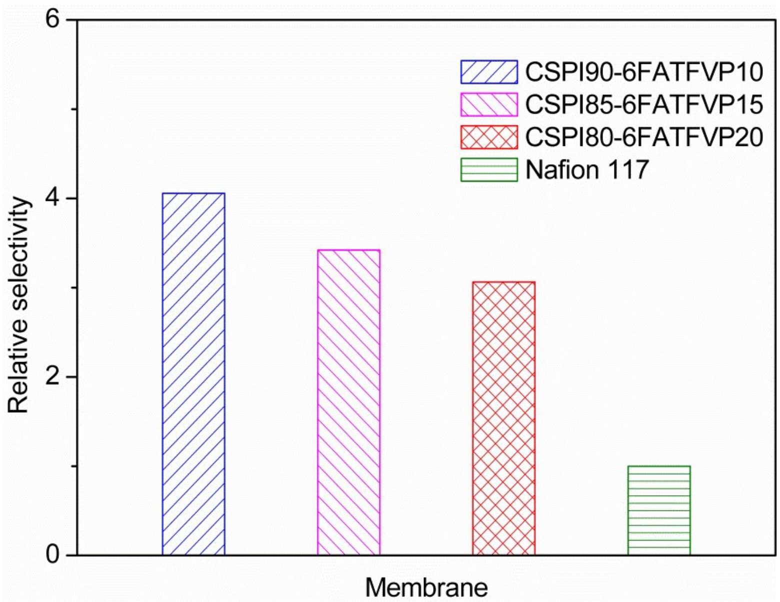

Fig. S4 The relative selectivity of CSPI-6FATFVPs membranes at room temperature. (Relative selectivity = selectivity of CSPI-6FATFVPs membranes/ selectivity of Nafion 117 membrane, selectivity = proton conductibity/ methanol permeability).

C. Supplementary Tables

Table S1 Intrisic viscosity, IEC_w and IEC_v of CSPI-6FATFVPs.

Copolyimide	ODADS (mol%)	6FATFVP (mol%)	η (dL g^{-1})	IEC_w[a] (meq.g^{-1})	IEC_w[b] (meq.g^{-1})	$IEC_{v(dry)}$ (meq.cm^{-3})	$IEC_{v(wet)}$ (meq.cm^{-3})	$IEC_{v(wet)}$ (meq.cm^{-3})
							RT[c]	80 °C[d]
CSPI90-6FATFVP10	90	10	0.95	2.74	2.41	3.61	2.71	2.37
CSPI85-6FATFVP15	85	15	0.87	2.52	2.28	3.46	2.96	2.52
CSPI80-6FATFVP20	80	20	0.91	2.31	2.07	3.09	2.91	2.56

[a] Theoretical value. [b] Determined by titration. [c] Calculated according to WU data at room temperature. [d] Calculated according to WU data at 80 °C.

Table S2 Swelling ratio, Proton conductivity, Oxidative stability and Tensile property of the SPIy-6FATFVPx membranes.

Copolyimide	Swelling ratio[a] (L%)		σ[a] (mS cm^{-1})		Oxidative stability (h)[b]	Tensile strength[c] (MPa)	Elongation at break[c] (%)
	RT	80 °C	RT	80 °C			
SPI90-6FATFVP10	24.5	-[d]	107	188	0.5	53(3)	8(16)
SPI85-6FATFVP15	18.7	-[d]	71	146	1.3	58(7)	8(13)
SPI80-6FATFVP20	17.2	-[d]	63	132	1.3	62(9)	6(13)

[a] Measured in fully hydrated state. [b] The time at which the membranes dissolved completely in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. [c] The tensile property measured at room temperature and the data in the parentheses relate to the tensile property of wet membranes. [d] Cannot be measured.

D. Supplementary References

1 J. H. Fang, X. X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita and K.Okamoto, Macromolecules, **2002**, 35, 9022-9028.

2 T. J. Peckham, J. Schmeisser and S. Holdcroft, J. Phys. Chem. B., 2008, 112, 2848-2858.