

Electronic Supplementary Information (ESI)

Ultra-High Proton Conduction in Electrospun Sulfonated Polyimide Nanofibers

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1. Experimental Methods

1.1. Materials

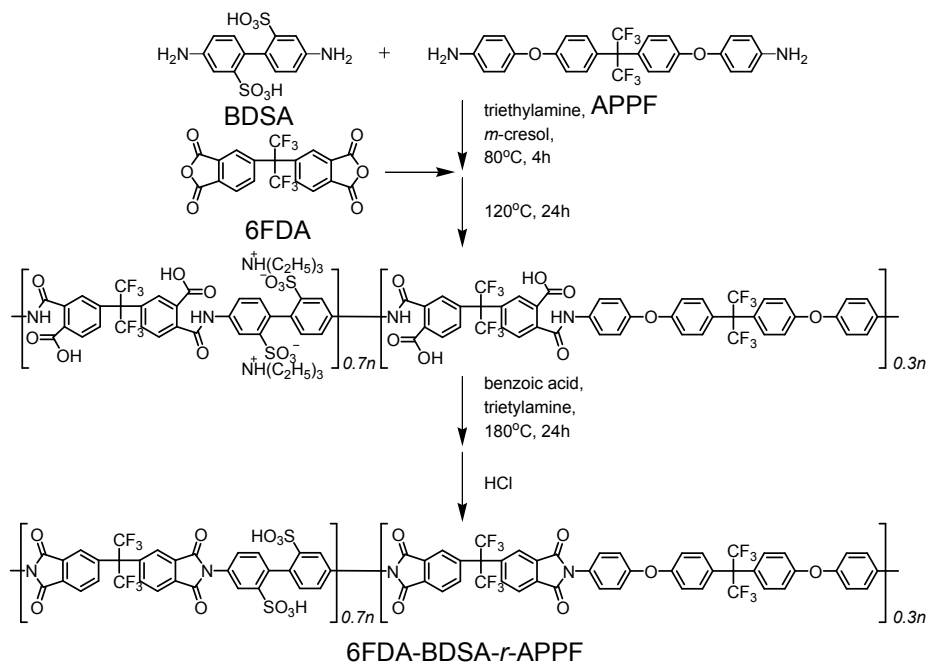
2,2'-Bis(3,4-dicarboxyphenyl)hexafluoro propane dianhydride (6FDA) was purchased from Central Glass Co. (Saitama, Japan) and was purified by sublimation before use. 4,4'-Diaminobiphenyl-2,2'-disulfonic acid (BDSA) was purchased from Tokyo Kasei Co. (Tokyo, Japan) and was purified by dissolution in a triethylamine aqueous solution and then precipitated in 1N H₂SO₄. Finally, the BDSA was dried in a vacuum oven at 80°C for 12 h. 2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (APPF) was purchased from Wako Chemical Ind. (Osaka, Japan) and was recrystallized twice from an ethanol solution prior to use. Other reagents were purchased from Kanto Chemical (Tokyo, Japan) and were used as received.

1.2. Synthesis of sulfonated polyimide (SPI)

The sulfonated polyimide, 6FDA-BDSA-*r*-APPF, was synthesized as follows (Scheme S1): In a three-neck round bottom flask, APPF (1.66 g, 3.21 mmol) and BDSA (2.58 g, 7.49 mmol) were dissolved in *m*-cresol (30 ml) in the presence of triethylamine (TEA, 6.0 ml) at 80°C for 4 h, and 6FDA (4.75 g, 10.7 mmol) was added to the solution. After stirring the solution at 120°C for 24 h, benzoic acid (1.46 g, 12.0 mmol) were added, and then stirred 180°C for 24 h. The molar ratio of BDSA to APPF was set at 7:3. The SPI (TEA form) was precipitated into ethyl acetate, washed several times with fresh ethyl acetate, and dried under vacuum at 150°C for 12 h. The polymer structure was characterized by ¹H NMR. The molecular weights (M_w and M_n) of the sulfonated

copolyimide were determined by gel-permeation chromatography (detector: Jasco 830-RI monitor) using two Shodex SB-806HQ and SB-804 HQ columns. Dimethylformamide containing 0.01 M lithium bromide was used as the eluent at a flow rate of 1.0 ml min⁻¹. The molecular weights were estimated by comparing the retention times on the columns to those of standard polystyrene. Ion exchange capacity (IEC) of SPI was measured by classical titration using NaCl and NaOH solutions after acid treatment in 0.1M hydrochloric acid for 24 h.

Its ¹H-NMR spectrum indicated successful synthesis of the objective sulfonated polyimide with triethylammonium counter ions. The SPI was soluble in aprotic polar solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and *N*-methylpyrrolidone (NMP), though it had high molecular weights ($M_w = 3.4 \times 10^5$, $M_w/M_n = 1.8$).



Scheme S1 Synthesis of sulfonated polyimide (6FDA-BDPA-r-APPF)

1.3. Preparation of uniaxially-aligned electrospun SPI nanofibers

The experimental set-up used for the preparation of the uniaxially-aligned SPI nanofibers is shown in Figure 1. The nanofibers were fabricated using an electrospinning apparatus (Fuence, Co., Ltd., ES-1000, Tokyo, Japan). A collector for uniaxially-aligned nanofibers was simply fabricated by using two conductive aluminum foils and a glass plate insulator. Width of both aluminum foils were 1 cm, and between the two aluminum foils were placed on the glass plates with their gap length of 3 cm. The electrospinning was carried out as follows: First, SPI (TEA form) was dissolved in anhydrous DMF with a concentration of 24wt%, and the polymer solution was loaded into a 1 ml syringe as the spinneret. A syringe pump was used to squeeze out the polymer solution at a constant speed (20 μ L/min) through a needle with an inner diameter of 0.21 mm. The distance between the spinneret and the collector was 10 cm. V_1 is the applied voltage between the spinneret and the collector, and was fixed to be 15 kV. On the other hand, the applied voltage between the two aluminum electrodes (V_2) was changed from 0.5 kV to 3.0 kV. The uniaxially-aligned SPI nanofibers with 146 ± 28 nm diameters by V_2 voltage of 0.5 kV (Table 1 run 4) was also prepared by tuning the electrospinning parameters, especially by setting V_1 voltage to be 20 kV. Uniaxially-aligned nanofibers were deposited between the opposed aluminum electrodes on the glass collector. The amount of the uniaxially-aligned nanofiber was controlled by the electrospinning deposition time. Finally, vacuum drying was carried out at 80°C for 12 h to remove the residual solvent from the fabricated nanofibers. Then, the SPI nanofibers were acidified with a 0.1 M HCl solution for 24 h to obtain SPI (proton form) nanofibers, and were dried under vacuum at 80°C for 12 h.

The size and morphology of electrospun uniaxially-aligned nanofibers were controlled by the electrospinning conditions, such as applied voltage (V_1) between the spinneret and the collector, applied voltage (V_2) between the two parallel electrodes, viscosity and feeding rate of the polymer solution, distance between the spinneret and the grounded plate collector, and a relative humidity (RH) in the apparatus.

The nanofibers were observed using a scanning electron microscope (SEM, JXP-6100P, JEOL, Tokyo, Japan). To determine the diameter, at least five pictures and 25 nanofibers were used.

1.4. Proton conductivity measurement

Proton conductivity of the SPI membrane was measured using electrochemical impedance spectroscopy over the frequency range from 50 Hz to 500 kHz (Hioki 3532-50, Tokyo, Japan) as reported in previous papers.¹⁰ In brief, a membrane ($1.0 \times 3.0 \text{ cm}^2$) and two blackened platinum plate electrodes were placed in a Teflon cell. The distance between the two electrodes was 1.0 cm. The impedance (R) of the membrane was measured in a thermo-controlled humidity chamber under various temperature (90- 30°C) and humidity (95-30%RH) conditions. Proton conductivity (σ) was calculated from Eq. (1):

$$\sigma = \frac{d}{A \cdot R} \quad (1)$$

where A and d are the conducting area of the membrane and the distance between the electrodes, respectively.

On the other hand, proton conductivity of SPI nanofiber was measured as follows: First, a hand-made micro-gap gold electrode, which was fabricated by cutting off sputtered gold thin layer to make a linear gap with ca. 75 μm -width on a glass plate. The uniaxially-aligned nanofibers on the collector were impressed on the micro-gap gold electrode to bridge the two electrodes with the uniaxially-aligned nanofibers. Impedance of the uniaxially-aligned nanofibers was similarly measured by the electrochemical impedance spectroscopy. Conducting area (A) of uniaxially-aligned nanofibers on the electrode was estimated from fiber cross-sectional area of a single nanofiber (a), which was calculated from average fiber diameter observed by SEM, and numbers of nanofibers on the electrode (N), which was counted by SEM observation. The conventional equation was converted to a modified Eq. (2):

$$\sigma = \frac{d}{(a \cdot N) \cdot R} \quad (2)$$

to calculate proton conductivity (σ) of the uniaxially-aligned nanofibers.

1.5. Water uptake measurement

In order to obtain enough weight of nanofibers for gravimetric measurement, electrospinning was carried out for long time under the same conditions to prepare the SPI nanofibers ($V_2 = 3.0 \text{ kV}$). The nanofibers were obtained as nanofibrous membrane, not as the aligned nanofibers, due to the decrease of the electrostatic attractive force between the two parallel electrodes, which were covered with massive amount of electrospun nanofibers. Water uptake of the SPI nanofibers

(nanofibrous membrane) and the SPI membrane were gravimetrically measured from the dried and humidified samples. The samples were dried in a vacuum oven at 80°C for 24 hr and then put in a thermo-controlled humidity chamber at 90°C and various relative humidity (90, 60, and 30%RH) for 24 h. After 24 hr, the samples were quickly weighed. The water uptake was calculated using Eq.

(3):

$$W(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

where W_s and W_d are the weights of the wet and dry samples, respectively.

1.6. Polarized ATR FT-IR spectroscopy

Polarized ATR FT-IR spectra were taken by FT-IR 6100 (JASCO, Tokyo, Japan) equipped with a polarized ATR accessory (ATR PRO 450-S, Prism: Ge). The uniaxially-aligned nanofibers were set along to the IR incident axis on the sample stage. The resolution and accumulations were set 4 cm^{-1} and 64, respectively.

2. SEM images of the SPI nanofibers

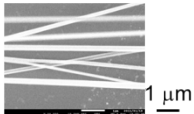
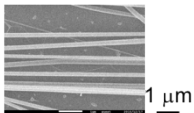
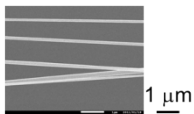
V_2 (kV)	SEM images	Fiber diameter (nm)	n (μm^{-1})
0.5		223 ± 43	2.2 ± 0.9
1.0		145 ± 29	2.4 ± 0.6
3.0		108 ± 22	1.7 ± 0.5

Fig. S1 SEM images, fiber diameters, and average numbers of nanofibers per 1 μm width (n) of the uniaxially-aligned SPI nanofibers prepared from different electrospinning conditions ($V_2 = 0.5, 1.0,$ and 3.0 kV).

3. Typical Nyquist plots of impedance measurement on the SPI nanofibers

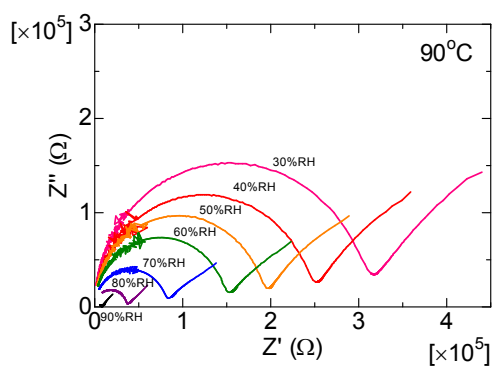


Fig. S2 Typical Nyquist plots of impedance measurement on the SPI nanofibers ($V_2 = 3.0$ kV)

4. Water uptake of the SPI nanofibers and membrane

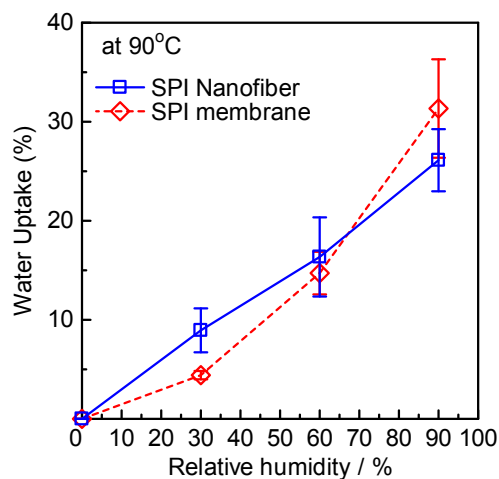


Fig. S3 Water uptake of the SPI nanofibers and membrane as a function of relative humidity at 90°C.

5. FT-IR peak assignment of SPI nanofibers

Typical peaks in Figure 3(a) attributed to the C=O symmetric stretch at 1720 cm^{-1} , C=C ring stretch at 1502 and 1471 cm^{-1} , C-O-C asymmetric stretch at 1239 cm^{-1} , S=O asymmetric stretch at 1191-1172 cm^{-1} , C-O-C symmetric stretch at 1096 cm^{-1} , and S=O symmetric stretch at 1037 cm^{-1} .