

Supplementary information for

Synthesis of superacid-modified poly(arylene ether sulfone)s via post-bromination

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Experimental details

Measurements

¹H and ¹⁹F NMR experiments were performed on a JEOL JNM-ECA 500 spectrometer using deuterated dimethyl sulfoxide (DMSO-*d*₆), deuterated chloroform (CDCl₃) or deuterated tetrachloroethane (C₂D₂Cl₄) as the solvent. Tetramethylsilane (TMS) was used as the internal standard for ¹H NMR spectra. Molecular weight measurements were performed with a Jasco PU-2080 Plus gel permeation chromatography system equipped with two columns (Shodex K-805L and K-806L) and a Jasco MD-2010 Plus multi-wavelength UV detector. *N,N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL/min. *M*_w and *M*_n were calibrated with standard polystyrene samples.

Ion exchange capacity (IEC)

A piece of FSPE-1 membranes was equilibrated in a large excess of 0.2 M NaCl aqueous solution for 15 h. The amount of HCl released from the membrane samples was determined by titration with aqueous 0.01 N NaOH using KEM Automatic Potentiometric Titrator AT-510.

Oxidative stability

A small piece of membrane samples was soaked in Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C for 1 h. The stability was evaluated by the changes in molecular weight, IEC, and weight of the test samples.

Hydrolytic stability

A small piece of membrane samples was treated at 140 °C and 100% RH in a closed, pressurized vial for 24 h. The stability was evaluated by the changes in molecular weight, IEC, and weight of the test samples.

Mechanical strength

Tensile testing was performed with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a chamber in which temperature (80 °C) and humidity (60% RH) were controlled by flowing humidified air with a Toshin Kogyo Bethel-3A temperature/humidity control unit. Stress-strain curves were obtained at a stretching rate of 1 mm/min for samples cut into a dumbbell shape (DIN- 53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)).

STEM observation

The membranes were stained with lead ions by ion exchange of the sulfonic acid groups. The membranes were immersed overnight in 0.5 M $\text{Pb}(\text{CH}_3\text{COO})_2$ aqueous solutions, rinsed with water, and dried in vacuum at 80 °C for 15 h. The stained membranes were embedded in epoxy resin and sectioned to give a 90 nm thick membrane. The images were taken on a Hitachi H-9500 scanning transmission electron microscope with an accelerating voltage of 300 kV.

Water uptake and proton conductivity

Water uptake and proton conductivity of the FSPE-1 membranes were measured with a Bel Japan MSB-AD-V-FC solid electrolyte analyzer system equipped with a chamber, a magnetic suspension balance, and a four-point probe conductivity cell. For water uptake measurements, membrane samples (50 - 60 mg) were placed in a chamber and dried at 80 °C under vacuum for 3 h until constant weight as a dry material was obtained. The membranes were then equilibrated with N_2 gas at given temperature and humidity for at least 1 h before the gravimetry was carried out. For the proton conductivity measurements, membrane samples (1.0 cm wide and 3.0 cm long) were placed in the same chamber. The samples were contacted with two gold wire outer current-carrying electrodes and two gold wire inner potential-detecting electrodes. Impedance measurements were carried out using a Solartron 1255B frequency response analyzer and Solartron SI 1287 potentiostat. The instrument was used in the potentiostatic mode with an AC amplitude of 300 mV and a frequency range from 1 to 100,000 Hz.