Supplementary information

Tuning hydrophobic composition in terpolymer-based anion exchange membranes to balance conductivity and stability

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Measurements

¹H and ¹⁹F NMR spectra were obtained on a JEOL JNM-ECA/ECX500 using deuterated chloroform (CDCl₃), 1,1,2,2-tetrachloroethane (TCE- d_2), or dimethylsulfoxide (DMSO- d_6) as a solvent. Tetramethylsilane (TMS) or the solvent was used as an internal reference. Molecular weight was measured with gel permeation chromatography (GPC) equipped with a Shodex K-805 L column and a Jasco UV 2077 detector (270 nm) with CHCl₃ containing 0.03 M triethylamine as eluent. Molecular weight was calibrated with standard polystyrene samples (ranged from $M_n = 1.26$ to 423 kDa, 10 samples).

Ion exchange capacity (IEC) was determined by titration. A membrane sample (ca. 20 mg) in chloride ion form was immersed in 0.2 M NaNO₃ (12.5 mL) at r.t. for 24 h. The amount of chloride ions released from the membrane was titrated with 0.01 M AgNO₃ using K_2CrO_4 as an indicator and NaHCO₃ as a pH adjuster.

For transmission electron microscopic (TEM) observation, membrane samples were stained with tetrachloroplatinate ions by ion exchange of the ammonium groups in 0.5 M K_2PtCl_4 aqueous solution at 40 °C for 24 h, rinsed with deionized water at r.t. for 24 h, and dried in a vacuum oven overnight. The stained membrane was embedded in an epoxy resin, sectioned to 50 nm thickness with a Leica microtome Ultracut UCT, and placed on a copper grid. Images were taken on a Hitachi H-9500 transmission electron microscope with an accelerating voltage of 200 kV. SAXS profiles were collected using a Nano-

Viewer (Rigaku) with Cu(K α) as an X-ray source. SAXS measurement was performed at 40 °C under nitrogen atmosphere humidified at 30 - 90% RH. The humidity was controlled by mixing vapor and dry gas with an external humidifier. The membrane sample in chloride ion form was placed in an SAXS cell and equilibrated in the humidified nitrogen for 2 h before the measurement.

Hydroxide ion conductivity of the membranes was measured in degassed, deionized water (18 MΩ) at 30, 40, 60, and 80 °C using a 4-probe conductivity cell attached with an AC impedance spectroscopy (Solartron 1255B, Solartron Inc.). Ion conducting resistance (R (Ω)) was determined from the impedance plot obtained in the frequency range from 1 to 10⁵ Hz. The hydroxide ion conductivity (σ) was calculated from the equation, $\sigma = l/AR$, where A (cm²) and l (cm) are the cross-section area of the membrane and the distance between two reference electrodes, respectively.

The water uptake was calculated using the following equation: Water uptake (%) = $(W_w - W_d)/W_d \times 100$, where W_w is the wet weight and W_d the dry weight (dried in a vacuum oven at 50 °C overnight) of the membrane.

Gas permeability of the membranes was measured using a GTR-110XADF gas permeability measurement apparatus (GTR TEC Co., Ltd.). A membrane sample in methyl sulfate ion form (45 mm in diameter and ca. 50 µm thick) was set in a cell that had gas inlet and outlet on both sides of the membrane. Prior to the measurement, both sides were exhausted by vacuum pump for 10 h. Then, test gas was supplied at a pressure of 201.30 kPa. The change of the pressure on the other side of the membrane was monitored for 10 min. The temperature was set at 80 °C throughout the measurement. The gas permeability coefficient, Q (cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹) was calculated from the following equation: $Q = dp/dt \times (V \times 273)/(760 \times (273+T)) \times 1/A \times 1/P \times I$, where dp/dt is a slope of the pressure-time plot, V (cm³) is the volume of the cell in low pressure side, T(K) is the absolute temperature, A (cm²) is the permeation area, P (cmHg) is the pressure of applied gas and l (cm) is the thickness of the membrane. The gas diffusion coefficient D (cm² s⁻¹) was calculated from the following equation: D = $l^2/6\theta$, where θ is the delay time, l (cm) is the thickness of the membrane. Using the gas permeability coefficient Q and diffusion coefficient D, the gas solubility coefficient S (cc cc⁻¹ cmHg⁻¹) was calculated from the following equation: S = Q/D.

Dynamic mechanical analysis (DMA) was carried out with an ITK DVA-225 dynamic viscoelastic analyzer (IT Measurement Control Co., Ltd.). Temperature dependence of storage modulus (E' (Pa)), loss modulus (E" (Pa)), and tan δ (= E''/E') at 60% RH and 10 Hz was measured for the membranes in chloride ion forms (5 × 30 mm) between r.t. and 100 °C at a heating rate of 1 °C min⁻¹. Humidity dependence of E', E", and tan δ at 80 °C and 10 Hz was also measured between 0% and 90% RH at a humidifying rate of 1%RH min⁻¹.

Tensile strength testing was carried out with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a temperature and humidity controllable chamber. A membrane sample in chloride ion form was cut into a dumbbell shape (35×6 mm (total) and 12×2 mm (test area)). Stress versus strain curves were obtained at 80 °C and 60% RH at a stretching rate of 10 mm min⁻¹ after equilibrating the membrane at least for 3 h. The humidity was controlled by mixing vapor and dry gas with an external humidifier.

Alkaline stability test of the membranes was performed in 8 M or 10 M KOH aqueous solution at 80 °C. The hydroxide ion conductivity was recorded in degassed water at 40 °C as a function of the testing time. Post-test analysis was performed by NMR spectra, titration, tensile strength testing.



Fig. S1 Time course of the hydroxide ion conductivity of QBPA-1 membrane in 10 M KOH aqueous solution at 80 °C.

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Fig. S2 Photograph of QBPA-1 membrane with IEC = 1.56 meq. g⁻¹ after the stability test in 8 M KOH aqueous solution for 1000 h at 80 °C.



Fig. S3 Stress versus strain curves of QBPA-1,4 membranes in Cl⁻ form at 80 °C and 60% RH, before (dashed line) and after (solid line) the alkaline stability test.