

Supplementary information

Ladder-type sulfonated poly(arylene perfluoroalkylene)s for high performance proton exchange membrane fuel cells

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EXPERIMENTAL SECTION

Spectroscopy. ^1H (500 MHz) and ^{19}F (471 MHz) NMR spectra were obtained by a JEOL JNM-ECA 500 spectrometer using $\text{DMSO-}d_6$ as a solvent and tetramethylsilane as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained by a JASCO FT/IR-6100.

Titration. The ion exchange capacity (IEC) of the membranes was measured by acid/base titration at r.t. Ca. 20 mg of dry membrane was immersed in 2 M NaCl aqueous solution for 24 h at r.t., and then was titrated with standard 0.01 M NaOH aqueous solution.

Molecular weight measurement. Gel permeation chromatography (GPC) with a UV detector (Jasco 805 UV), a Shodex K-805L column and DMF containing 0.01 M LiBr as eluent was used to estimate molecular weight of the polymers. Measurement was conducted at 50 °C, and molecular weight was calibrated with standard polystyrene samples.

Morphology. For transmission electron microscopy (TEM), the membrane was stained in 0.5 M $\text{Pb}(\text{OAc})_2$ aqueous solution, embedded in epoxy resin, sectioned to 50 nm thickness and placed on copper grids. Images were obtained via Hitachi H-9500 microscope with an accelerating voltage of 200 kV.

Water uptake and proton conductivity. Water uptake and in-plane proton conductivity of the membranes were measured simultaneously at 80 °C with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) in a temperature/humidity-controllable chamber. The weight was measured by a magnetic suspension balance. The dry weight of a membrane was provided after drying at 80 °C in vacuum for 3 h and the wet weight was obtained after exposure to the testing humidity for more than 2 h. The water uptake was calculated from the equation: $(\text{wet weight} - \text{dry weight})/\text{dry weight} \times 100$. The in-plane proton conductivity was tested with a four-probe conductivity cell connected with an ac impedance analyzer (Solartron 1255B and 1287, Solartron Inc.). Ion-conducting resistance was obtained in the frequency range of 1 to 10^5 Hz. The proton conductivity

(δ) was calculated from the following equation: $\delta = l/(A \times R)$, where l is the distance between the two reference electrodes and A is the cross-sectional area.

Dynamic mechanical analysis (DMA). DMA was carried out with an ITK DVA-225 dynamic viscoelastic analyzer to evaluate the temperature (heating rate of $1\text{ }^{\circ}\text{C min}^{-1}$ from r.t. to $100\text{ }^{\circ}\text{C}$ at 60% RH) or humidity (humidification rate of $1\% \text{ RH min}^{-1}$ from 0 to 90% RH at $80\text{ }^{\circ}\text{C}$) dependence of the storage moduli (E'), loss moduli (E''), and $\tan \delta (= E''/E')$ of the membranes.

Tensile test. The tensile property was measured with a Shimadzu AGS-J 500N universal testing instrument attached with a Toshin Kogyo Bethel-3A temperature/humidity-controllable chamber at $80\text{ }^{\circ}\text{C}$ and 60% RH. Samples cut into a dumbbell shape [DIN-53504-S3, $35\text{ mm} \times 6\text{ mm}$ (total) and $12\text{ mm} \times 2\text{ mm}$ (test area)] were used. After equilibrating under the tested conditions for at least 2 h, the stress-strain curves were obtained at a stretching rate of 10 mm min^{-1} .

Preparation of catalyst-coated membrane (CCM). A catalyst paste was prepared by mixing Pt/CB catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo K. K.), Nafion dispersion (IEC = $0.95\text{--}1.03\text{ meq g}^{-1}$, D-521, Du Pont), deionized water and ethanol by ball milling for 30 min. The mass ratio of the Nafion ionomer to the carbon support (I/C) was adjusted to 0.7. Catalyst-coated membranes (CCMs) were prepared by spraying the catalyst paste on both sides of the membrane (SPAF-*m*P-Lad) by pulse swirl spray (PSS) technique. The CCMs were dried at $60\text{ }^{\circ}\text{C}$ overnight and hot-pressed at $140\text{ }^{\circ}\text{C}$ and 1.0 MPa for 3 min. The geometric area and the Pt loading amount in the catalyst layer (CL) were 4.41 cm^2 and $0.50 \pm 0.02\text{ mg cm}^{-2}$, respectively.

Fuel cell operation. Linear sweep voltammetry (LSV) was measured to evaluate the permeability of hydrogen gas from the anode to the cathode through the ionomer membranes. LSV measurement was carried out at 30 or 100% RH and $80\text{ }^{\circ}\text{C}$. Prior to the LSV measurements, H_2 (100 mL min^{-1}) and N_2 (100 mL min^{-1}) were supplied to the anode and the cathode, respectively. The cathode potential was swept from 0.15 to 0.6 V at a

sweep rate of 0.5 mV s^{-1} . To evaluate the cell performance, the polarization (IV) curves were measured at 30 or 100% RH and $80 \text{ }^\circ\text{C}$. Pure H_2 and O_2 (or air) were supplied to the anode and the cathode, respectively. The gas utilizations at the anode and the cathode were 70% and 40%, respectively. The high frequency resistance (HFR) of the cell was measured with an ac milliohmmeter (Model 3356 Tsuruga Electric Corporation) at 1.0 kHz. The open circuit voltage (OCV) hold test was carried out at $80 \text{ }^\circ\text{C}$ and 30% RH with H_2 for the anode and air for the cathode, respectively, at a gas flow rate of 100 mL min^{-1} . The OCV hold test was continued for 1000 h.

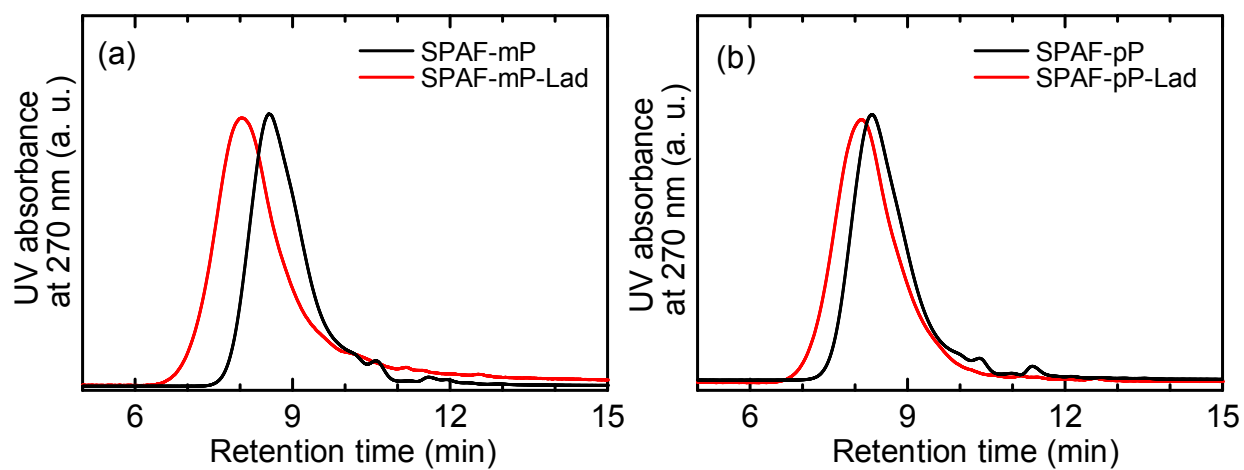


Figure S1. GPC profiles of (a) SPAF-*m*P and SPAF-*m*P-Lad and (b) SPAF-*p*P and SPAF-*p*P-Lad.

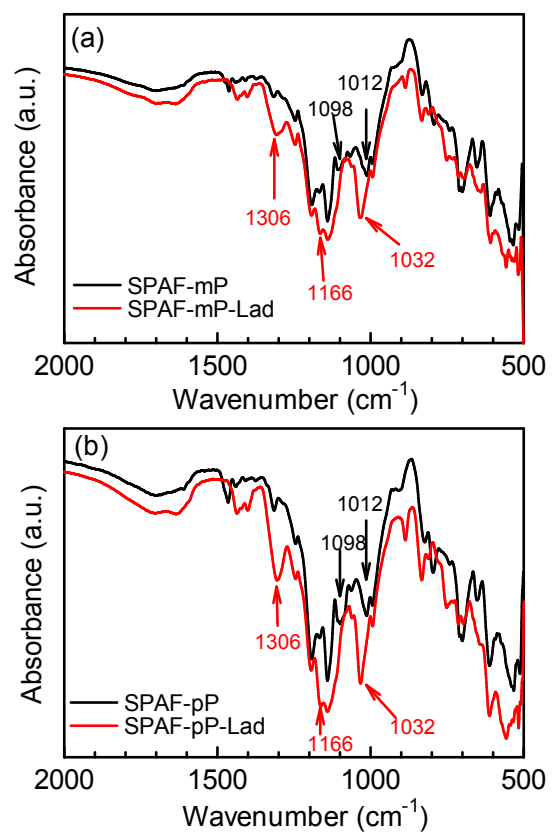


Figure S2. FT-IR spectra of (a) SPAF-*m*P and SPAF-*m*P-Lad and (b) SPAF-*p*P and SPAF-*p*P-Lad membranes.

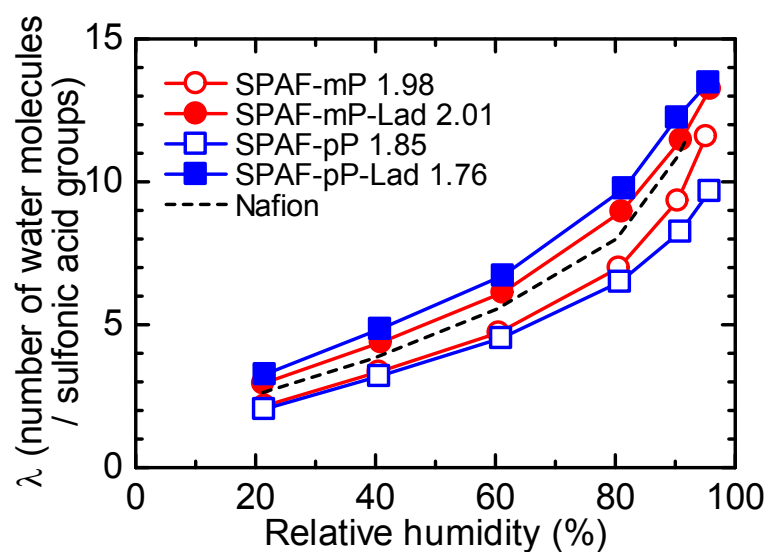


Figure S3. Relative humidity dependence of number of water molecules per sulfonic acid group for SPAF-P and SPAF-P-Lad membranes at 80 °C.

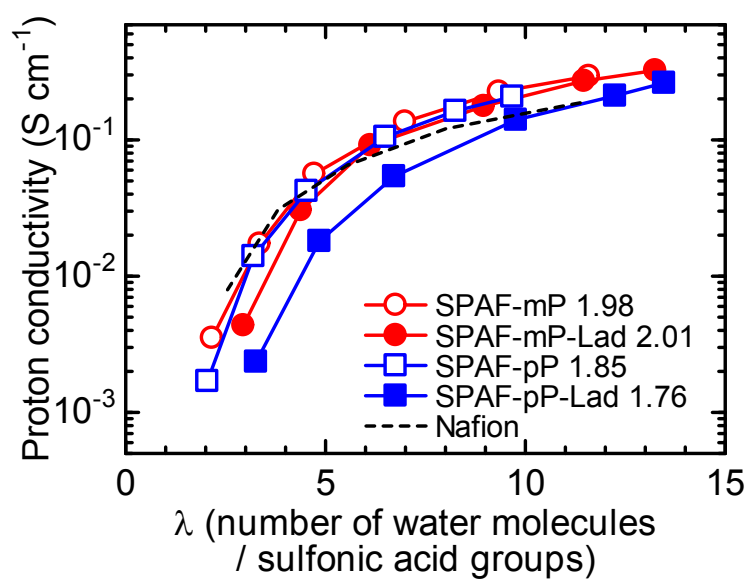


Figure S4. Proton conductivity of SPAF-P and SPAF-P-Lad membranes as a function of number of water molecules per sulfonic acid group at 80 °C

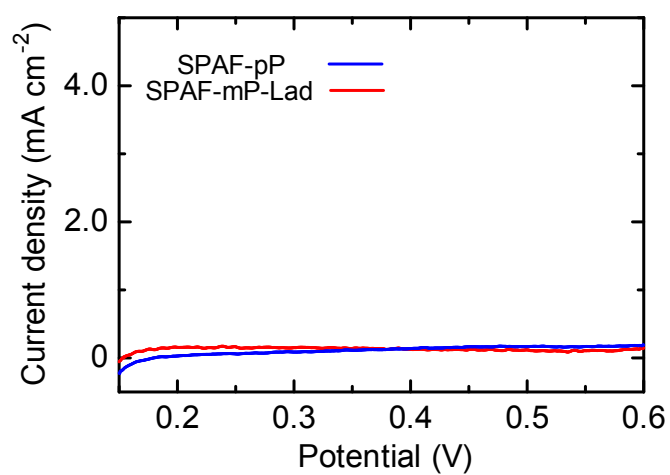


Figure S5. LSVs of SPAF-*p*P and SPAF-*m*P-Lad membranes at 80 °C and 100% RH.

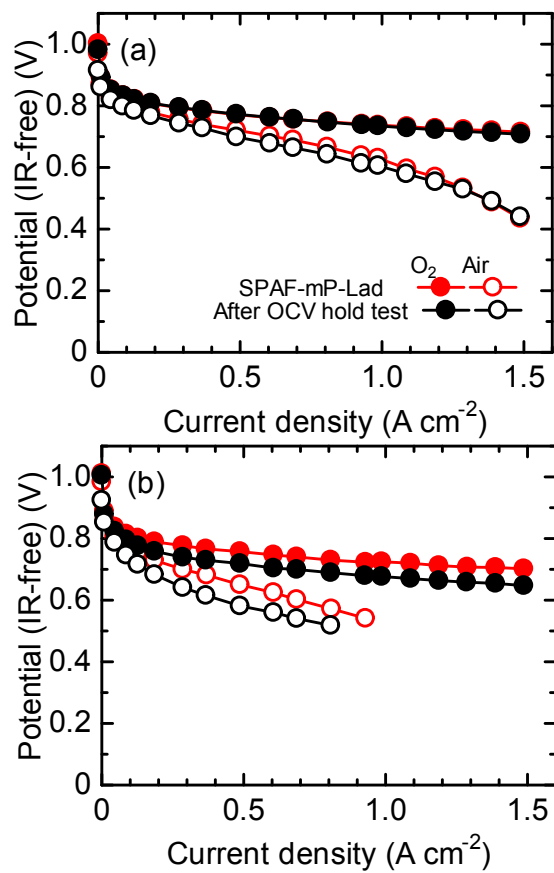


Figure S6. *IR*-free polarization curves for the SPAF-*mP*-Lad cell at 80 °C, (a) 100% and (b) 30% RH after OCV hold test for 1000 h.

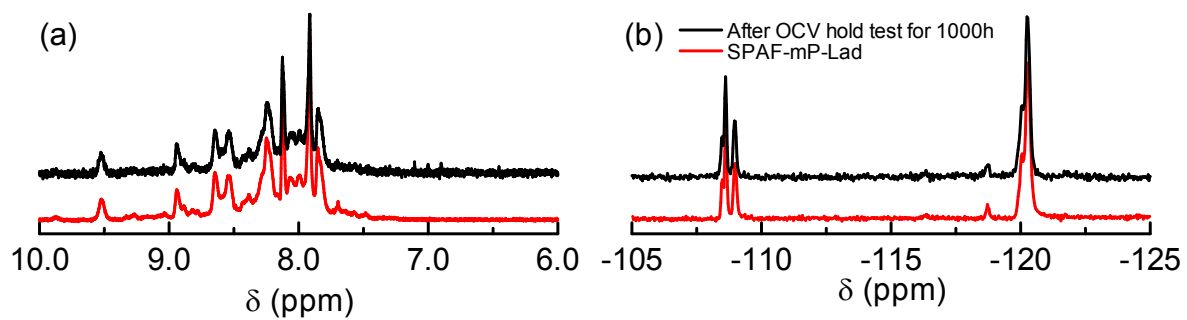


Figure S7. (a) ^1H and (b) ^{19}F NMR spectra of SPAF-*mP*-Lad membrane in $\text{DMSO-}d_6$ at $80\text{ }^\circ\text{C}$ before and after the OCV hold test for 1000 h

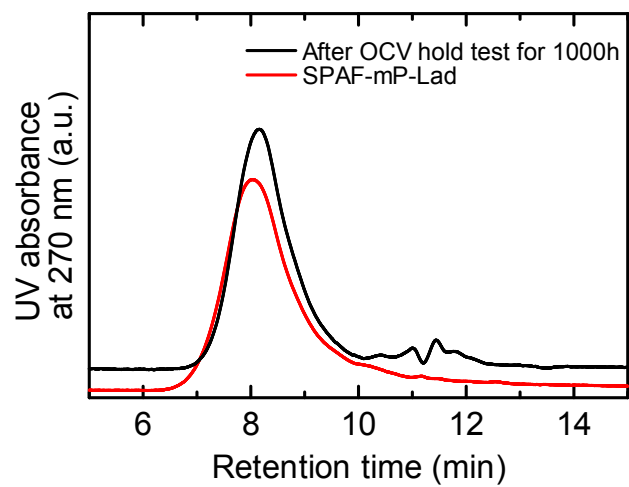


Figure S8. GPC profiles of SPAF-*mP*-Lad membrane before and after the OCV hold test for 1000 h.