Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Comb-Shaped Proton Exchange Membranes with Dangling Polystyrene Grafted onto PVDF for PEM Fuel Cells and Water Electrolysis

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SI 1: ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy

Bruker 500 MHz to spectrometer was used to record the ^{1}H NMR spectra. ^{1}H NMR spectra were recorded at 25 °C, using acetone-d6 as solvent for respective compounds and tetramethylsilane (TMS) as the internal reference.

SI 2: Attenuated Total Reflection Infrared (ATR-IR) spectroscopies

The prepared PEMs were dried in a vacuum oven at 40 °C for 24 h and subjected to the ATR-IR analysis. The area of 3×6 cm^2 of membrane sample was taken for ATR-IR analysis. ATR-IR of the membranes was recorded on an instrument (Spectrum 2, Perkin Elmer) at room temperature. A Germanium crystal, fixed at a 45^o angle of incidence, which gave a penetration depth of ~1 µ in the chemical infrared region, was used for recording the ATR-IR spectra. ATR-IR spectra on 5 different positions were recorded.

SI 3: Wide-angle XRD

Wide-angle XRD of the PEMs was determined in a powder XRD (Empyrean-PANalytical) instrument using a Cu Kα X-ray source operating at 40 kV and 20 mA with a scan rate of 0.033 ^{o}/min in the 2θ range of 5 ^{o} to 80 ^{o}. (Membrane sample 2 cm × 2 cm)

SI 4: Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM) analyses of the PEMs

The surface morphology of the composite PEMs was investigated in a field emission SEM (JEOL JSM-7100F) at an accelerated voltage of 15kV. AFM measurements of the blend PEMs were performed in semi-contact mode using a Ntegra Aura, (made by Nt-Mdt, Moscow) instrument at room temperature in air, employing “Nova” software for image analysis. Images were recorded from different areas of each sample. For AFM sample preparation, 10 mg of PEMs (sPSt-60, sPSt-45, sPSt-30) were dissolved in 10 mL dimethyl acetamide (DMAc) each. After complete dissolution, the solution was deposited on freshly cleaved mica and kept for 12 h at room temperature in $CaCl_2$ filled desiccator fitted with the outlet to slowly remove the solvent while avoiding moisture contact. Next, the coated mica was dried in an oven at 60 °C under a vacuum for 12 h for AFM analysis. TEM images were obtained with a transmission electron microscope (JEM 2100, JEOL) operated at an accelerated voltage of 80 kV. For TEM analysis, 10 mg PEM samples were dispersed 10 mL DMAc (same as AFM sample preparation) using an ultra sonicator, and the dispersed solution was carefully deposited on the carbon-coated copper grid (SPI Supplies, 300 mesh). The grid was then kept at a $CaCl_2$ filled desiccator fitted with an outlet for slow evaporation of the solvent and also to avoid moisture contact with the coated grid. Then the coated grid was heated at 80 $^{\circ}$C under vacuum for 12 h for TEM analysis.

SI 5: DSC analysis and the degree of crystallinity

DSC measurements of the PEMs were carried out in a Netzsch DSC 204 F1 Phoenix instrument. The data were analyzed with the help of proteus 6.1.0d software. Cyclohexane and indium were used for the calibration of the temperature scale. Vacuum dried samples (20 mg) were heated from -80 ^{o}C to +180 ^{o}C at the rate of 20 ^{o}C/min. The samples were then quenched to -80 ^{o}C at a rate of 20 ^{o}C/min after keeping it for 1 min at +180 ^{o}C and then the second heating was performed at a heating rate of 20 ^{o}C/min. The first run in DSC was necessary to remove the trace of moisture and to the homogenization of the sample. Glass transition temperature (T_g) was recorded as the inflection point of the heat-capacity jump from the second heating curve.

The degree of crystallinity (X_c) of the prepared PEMs was calculated using the following equation:

$$X_c = \left(\frac{\Delta H_m}{\epsilon . \Delta H_f^*}\right) \times 100 \qquad (S1)$$

Where, ΔH_m is the heat of fusion of the corresponding PEMs (area under the melting endotherm, J g^{-1}), ΔH_f^* corresponds to the heat of fusion of pure PVDF (where ΔH_f^* = 104.5 J g^{-1} when $X_c = 100$), and ϵ is the fractional ratio of PVDF present in the corresponding PEMs (1 for pure PVDF and 0.82 for the PEMs).

SI 6: Thermal stability of the PEMs by Thermogravimetric analysis (TGA)

TGA analysis was carried out using a Netzsch TGA (TG209 F1 Libra) system. The membrane samples were heated from 30 ^{o}C to 600 ^{o}C under a nitrogen atmosphere at a heating rate of 10 ^{o}C/min. The data was analyzed with the help of proteus 6.1.0d software.

SI 7: Dynamic mechanical analyzer (DMA)

The mechanical stability of the PEMs was determined from DMA analysis. DMA analysis was carried out in a Netzsch DMA system. Samples were heated from 30 ^{o}C to 250 ^{o}C at a heating rate of 3 ^{o}C/min at a frequency 1 Hz and a force of 1 N. The viscoelasticity and the T_g was determined from the loss modulus *vs.* temperature plots.

SI 8: Stress-strain property of the PEMs

Stress-strain property (stress and elongation at break) of membrane samples (4 cm long, 0.35 cm width) was determined using ISO 527 S2 method in a Zwick Roell Z2.5 tester. The speed used for the measurement was 20 mm/min. The testXpert II-V3.5 software was used for data analysis. Measurements were carried out with 4–5 sample films in the water-swollen state and in dry state, whose averages are reported. During measurements, the water content of the samples was maintained by placing wet tissue around the samples.

SI 9: Determination of Water Uptake and Swelling Ratio of the PEMs

Three pieces of each type of membrane sample (size: 3 cm × 3 cm) were dried in a vacuum oven. Then dry weight (W_d) of these pieces was measured and put in DI water for 24 h. After that, by removing the surface water by filter paper, the wet weight (W_w) of the pieces was obtained. The following equation was used to calculate the WU value.

$$Water\ uptake\ (\%) = \frac{W_w - W_d}{W_d} \times 100 \qquad (S2)$$

For the determination of swelling ratio, the change of length of the membranes at dry state (L_d) and wet state (L_w) were measured and calculated by the following equation:

$$Swelling\ ratio\ (\%) = \frac{L_w - L_d}{L_d} \times 100 \qquad (S3)$$

SI 10: Determination of contact angle

The water contact angle (θ_{WCA}) of the prepared PEM samples (2 cm × 8 cm, vacuum dried) was determined using KRÜSS Drop Shape Analyzer – DSA 25 instrument analyzed with KRÜSS ADVANCE 1.16.0.10201 software. The 'Sessile drop' measurement method was used with the gravitational acceleration of 9.80665 m/s².

SI 11: Determination of IEC of the PEMs

The IEC, defined as the ratio between the number of exchangeable ionic groups (equivalents) and the weight of dry membrane, was determined by the classical titration method. IEC of PEMs was measured by acid base titration method. Accurately weighted dry membranes were kept in 1 M HCl solution for 24 h then excessive HCl was washed off by DI water. After that, the membranes were put into 0.5 M NaCl solution to exchange the H^+ with Na^+. The amount of exchangeable H^+ was titrated with 0.01 M NaOH solution using phenolphthalein indicator.

At least three cycles of ion exchanging and regeneration were used to obtain a steady value. The averages of 3 cycles are reported here. IEC was calculated using the following eqn.:

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{Dry\ weight\ of\ PEM} \times \frac{V_{NaCl}}{V'_{NaCl}} \qquad (S4)$$

Where C_{NaOH} and V_{NaOH} are the concentration and volume of NaOH, V_{NaCl} is the volume of NaCl in which the membrane was kept and V'_{NaCl} is the volume NaCl which was used for titration.

If the PEM was kept in 50 ml of NaCl and if 10 ml of it was used for titration then the value of V_{NaCl} is 50 and the value of V'_{NaCl} is 10.

Hydration number (λ_{hyd}) of the membranes was calculated as:

$$\lambda_{hyd} = \frac{10\ \times WU}{18\ \times IEC} \qquad (S5)$$

SI 12: Determination of the proton conductivity and mobility of the PEMs

The surface area resistance of PEMs was measured in a potentiostat/galvanostat (Vionic model, Metrohm Autolab BV, The Netherlands) via the through-plane method. The membranes were placed in between two in-house made acrylic plates coated with circular carbon electrodes (having an effective area of 1 cm^2), which were kept in ultrapure water after conditioning in 0.5 M HCl for 12 h. Sinusoidal alternating current (AC) was supplied to the respective electrodes for recording the various resistances using the frequency range of 1 MHz to 10 Hz. The resistance was calculated using electrochemical circuit fitting with fit and simulation method. κ was calculated by using the following equation:

$$K^m = \frac{\Delta x}{A \times R} \qquad (S6)$$

For the K^m measurement in a hydrated state, the cell was dipped in ultrapure water, and for the measurements in a dry state, the cell was kept out of ultrapure water.

where Δx is the thickness of the wet membrane, R is the membrane resistance, and A is the effective electrode area.

The sulfonic acid content ([-SO_3H]) is determined using the following formula:

$$[-SO_3H] = \frac{mass\ of\ dry\ PEM\ sample \times IEC}{Volume\ of\ the\ PEM\ sample} \qquad (S7)$$

The effective proton mobility (μ_{eff}) was calculated as:

$$\mu_{eff} = \frac{K^m}{F \times [-SO_3H]} \qquad (S8)$$

Where, F is the Faraday constant, i.e., 96485 C/mol.

SI 13: Calculation of degree of sulfonation

The degree of sulfonation (w/w) with respect to total weight of polymer has been calculated using IEC, using the following equation.

$$DS\ (w/w) = \frac{IEC}{1000} \times M_{SSA} \times 100 \qquad \text{(S9)}$$

Where, M_{SSA} is the molar mass of one unit of styrene sulfonic acid (184.22 g).

For sPSt-60,

$$DS\ (w/w) = \frac{1.48\ meq/g}{1000} \times 184.22\ g \times 100$$

$$DS\ (w/w) = 27.26\ \%\ with\ respect\ to\ s(PVDF - g - PSt)\ \ polymer$$

SI 14: Activation energy (E_a) calculation

The E_a of the composite PEMs was calculated from their respective Arrhenius plots. The slope of the straight Arrhenius curve (b) was evaluated and the E_a was calculated using the following equation.

$$E_a = -b \times R \qquad \text{(S10)}$$

Where b is the slope and R is the gas constant (8.314 J/mol/K).

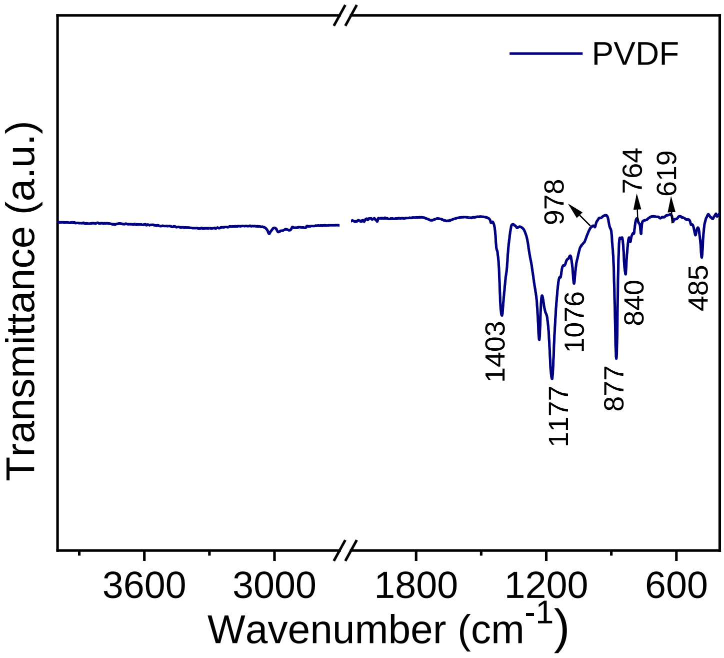


Fig. S1 ATR-IR spectra of PVDF.

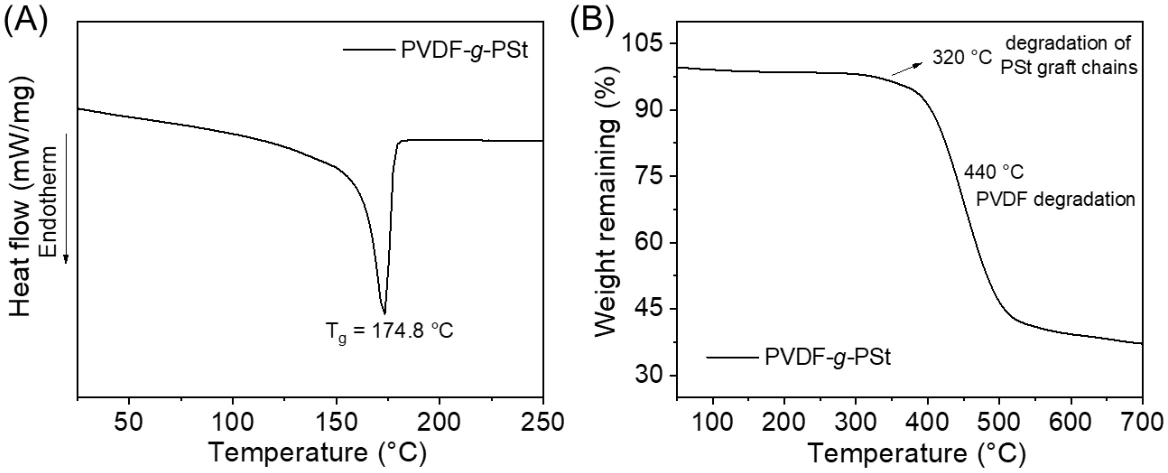


Fig. S2 (A) DSC and (B) TGA profile of pristine PVDF-*g*-PSt membrane.

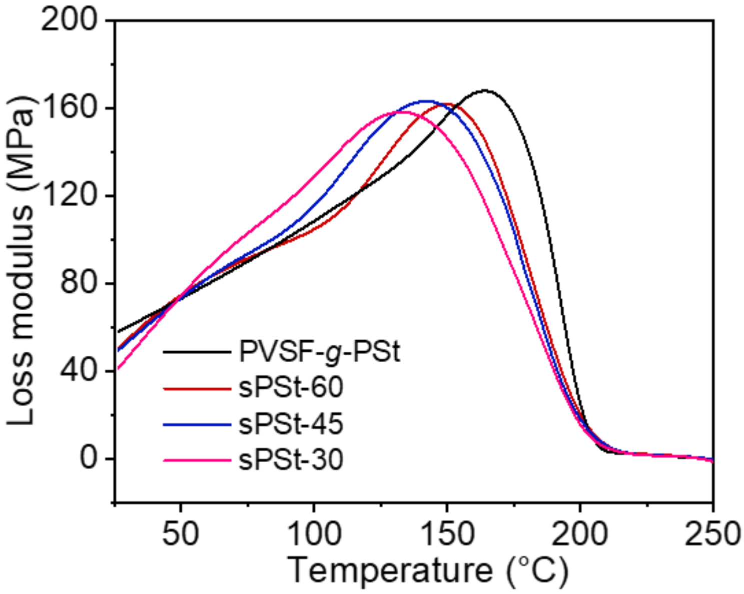


Fig. S3 loss modulus vs. temperature curve of the prepared PEMs.

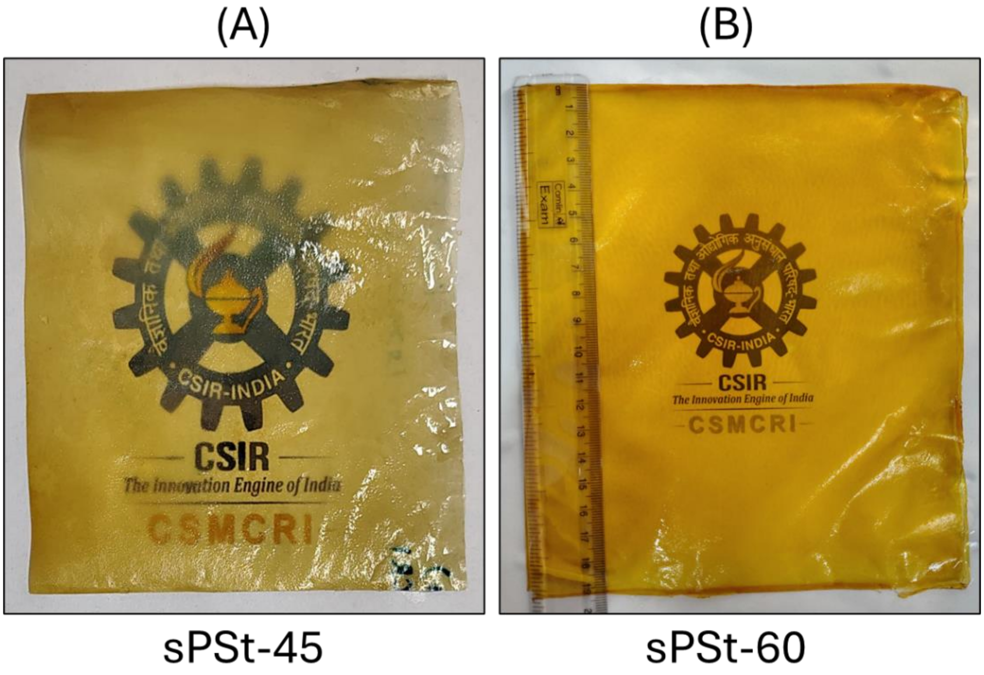


Fig. S4 Digital images of the PEMs.

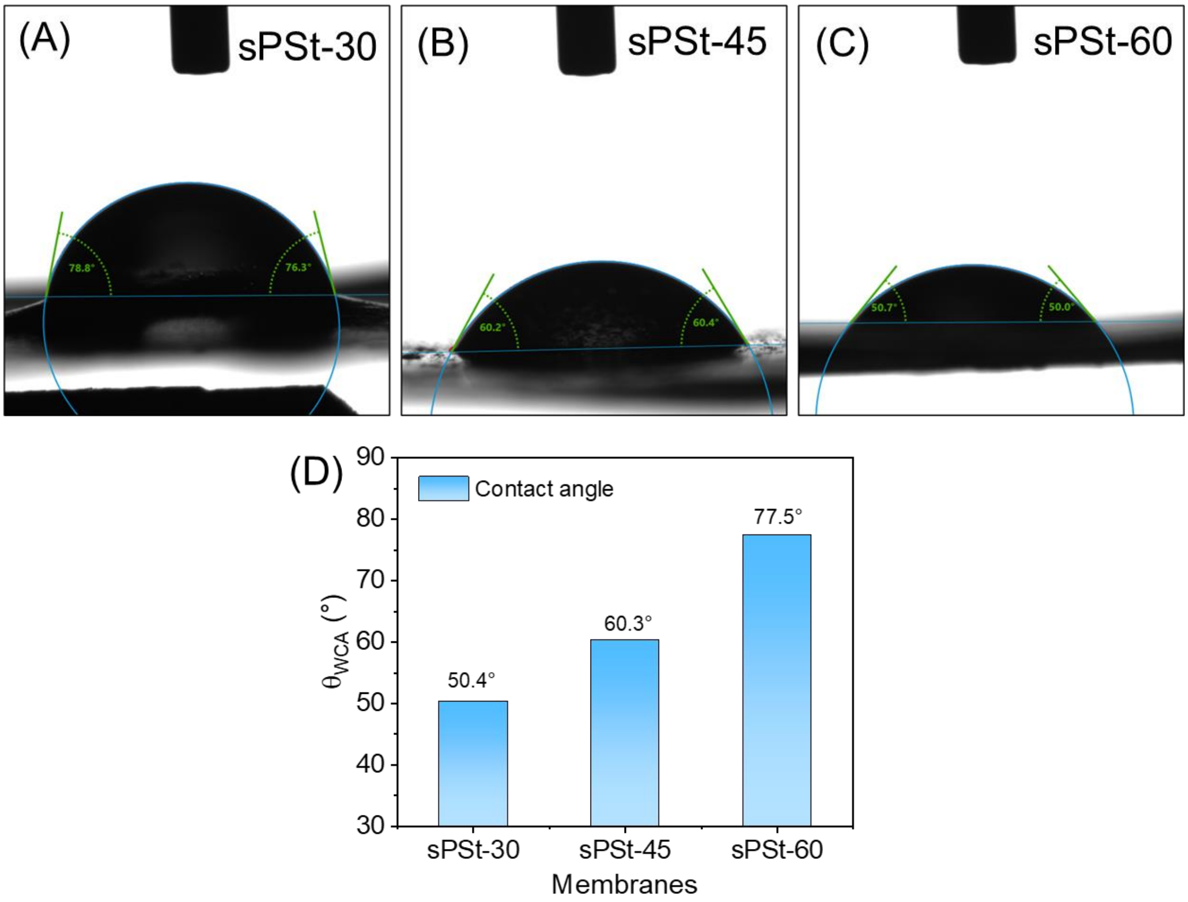
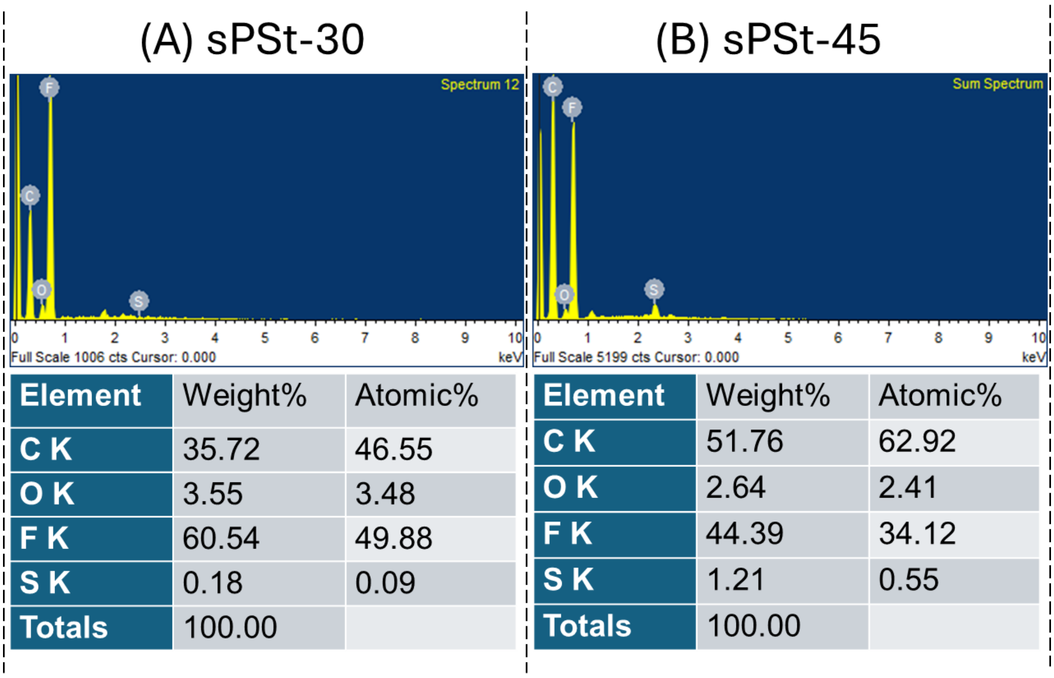


Fig. S5 Contact angle measurements of the prepared PEMs.



(A) sPSt-30

Element	Weight%	Atomic%
C K	35.72	46.55
O K	3.55	3.48
F K	60.54	49.88
S K	0.18	0.09
Totals	100.00	

(B) sPSt-45

Element	Weight%	Atomic%
C K	51.76	62.92
O K	2.64	2.41
F K	44.39	34.12
S K	1.21	0.55
Totals	100.00	

Fig. S6 EDX elemental mapping of sPSt-30 and sPSt-45.

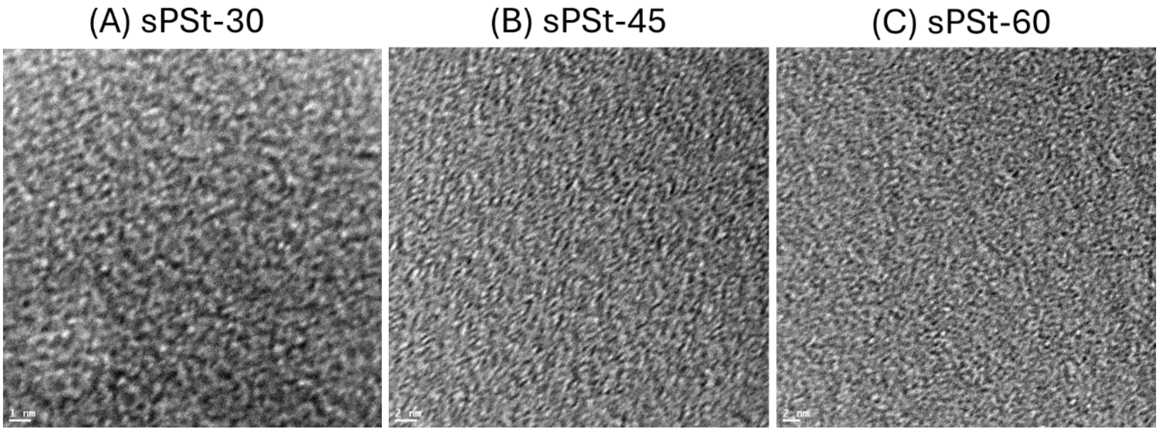


Fig. S7 TEM images of the PEMs.

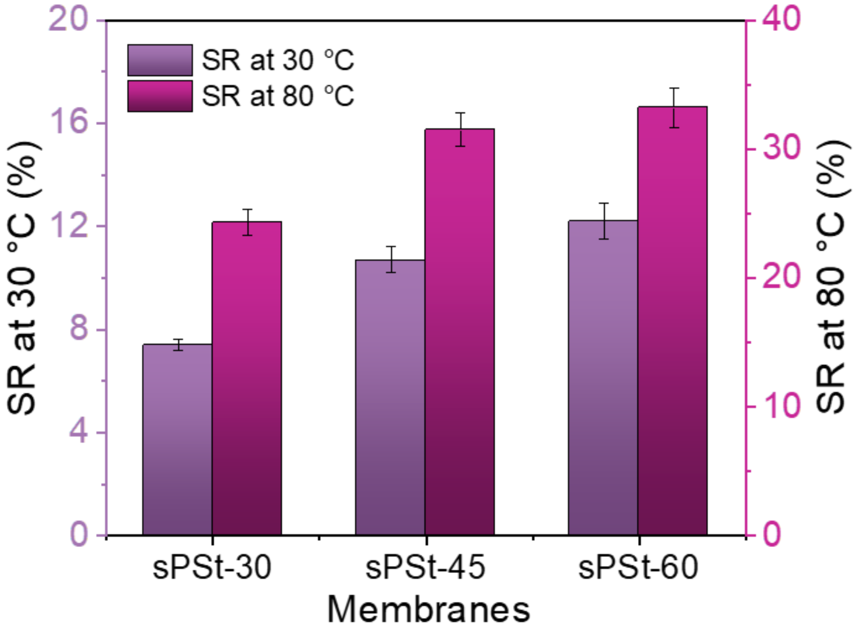


Fig. S8 Swelling ratio of the PEMs at 30 and 80 °C.

Fig. S9 Folding-unfolding of (A) sPSt-45 and (B) sPSt-60 showing mechanical flexibility.

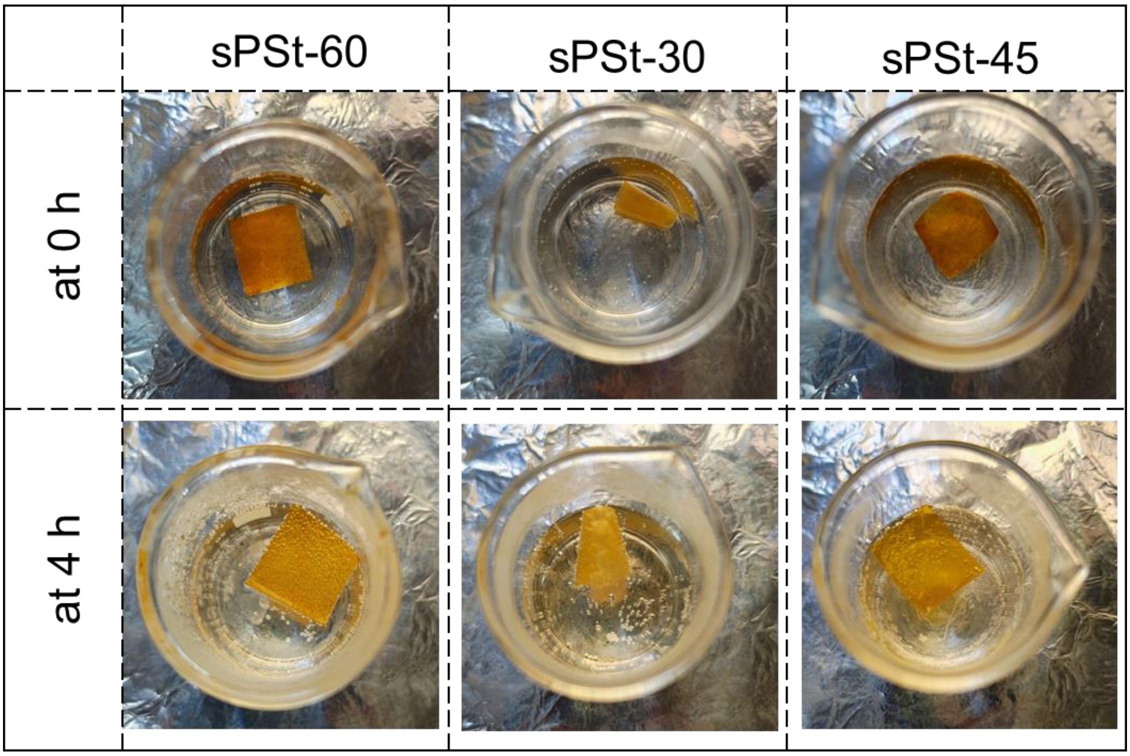


Fig. S10 Digital images of the PEMs during real-time Fenton’s test.

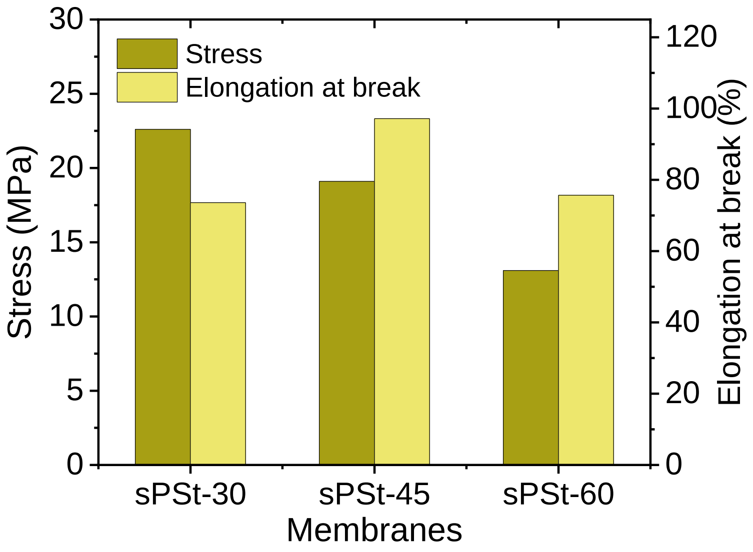


Fig. S11 UTM stress-strain analysis to assess hydrolytic stability of the PEMs.

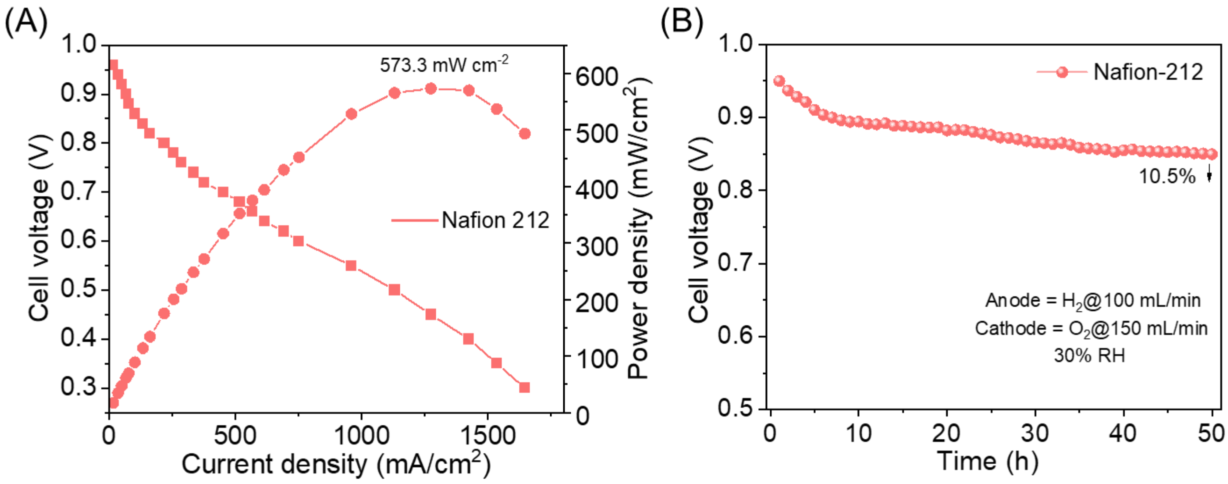


Fig. S12 (A) Polarization curve and (B) durability study of Nafion 212.

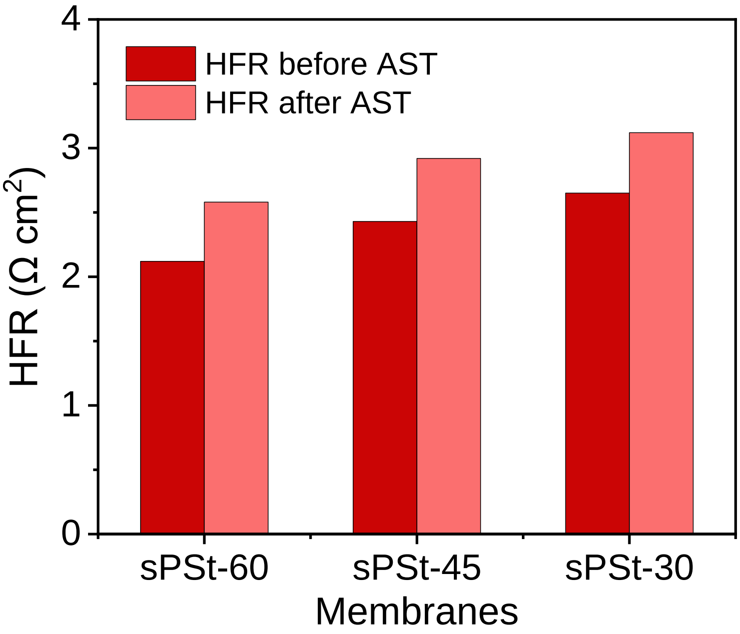


Fig. S13 HFR of the PEMs before and after AST (in PEMFC).

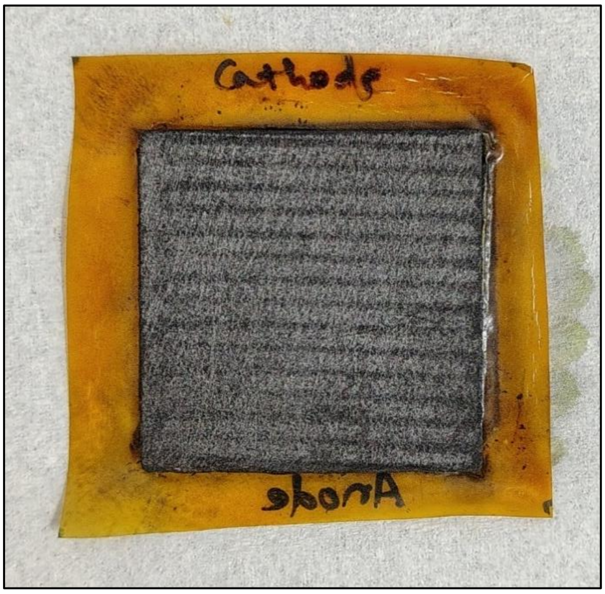


Fig. S14. sPSt-60-based MEA after durability test in PEMWE.

Table S1. Different resistance parameters determined from EIS fitting equations.

Membrane	*Ionic resistance (R_s, Ω)*	*Charge transfer resistance (R_{ct}, Ω)*	*Warburg resistance (R_w, Ω)*	*Interpretation*
sPSt-30	2.43	6.17	23.41	High overall resistance, sluggish charge transfer, and diffusion
sPSt-45	1.69	2.73	21.45	Moderate resistance, good balance between bulk and interfacial properties
sPSt-60	1.45	2.38	17.62	Best performer; low bulk, interfacial, and diffusion resistances

Notes: *The electrochemical impedance spectroscopy (EIS) data were fitted using NOVA 2.1 software connected to a Metrohm Vionic potentiostat. A Randles equivalent circuit was employed to evaluate key interfacial parameters, including ionic resistance, charge transfer resistance, and Warburg impedance*.