

Electronic Supplementary Information:

Highly Conductive, Crosslinked Ionomers Based on Poly(styrene-co-maleic anhydride) for Water Electrolysis

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Experimental Section

Materials

Poly(styrene-*co*-maleic anhydride) (styrene: maleic anhydride = 1:1, molecule weight: 350,000) was purchased from Elf Atochem. Dimethyl sulfoxide (DMSO, Tedia) was freshly distilled from calcium hydride before use. 2-Aminoethanesulfonic acid and sodium hydroxide (NaOH) were obtained from Sigma, while aminopropyltriethoxysilane (APTES) was supplied by Dow Corning Corporation. Bis-(aminopropyl)-poly(dimethylsiloxane) (BAPPDMS) (Mw: 900 g mol⁻¹) was obtained from the Shin-Etsu Corporation, and the hydrochloric acid (37%) was from Riedel-de Haën. The Nafion[®]-117 membrane was supplied from DuPont Fluoroproducts, while other chemicals including tetraethyl orthosilicate (TEOS), nitric acid (HNO₃, 69.5 wt.%), sodium chloride (NaCl), methanol (CH₃OH), and sulfuric acid (H₂SO₄)

were obtained from Aldrich. All aqueous solutions were prepared using deionized water purified through a Milli-Q system.

Membrane preparation

The synthesis of POSS-crosslinked sulfonated poly(styrene-*co*-maleic imide) is described as follows. Sodium aminoethanesulfonate (AESA-Na) was obtained by mixing aminoethanesulfonic acid (AESA) with equal molar NaOH in water at 60 °C for 12 h. Typical procedure for preparing the membrane is as follows: 1.5 g of SMA (7.4×10^{-3} equivalent of anhydride) was dissolved in 30 ml of dry DMSO in a three-necked flask at 80 °C equipped with a N₂ inlet. AESA-Na (2.47 mmol) was also dissolved in DMSO and mixed well. The temperature was kept at 80 °C. After 3 h, BAPPDMS (1.64 mmol) and APTES (1.64 mmol) in DMSO was added slowly into the mixture and vigorously stirred at 80 °C for another 3 h. Subsequently, 1.64 mmol of TEOS and 12.2 mmol of water were added and stirred for 1 h. The solution was then cooled to room temperature and concentrated by using a rotary evaporator. The viscous mixture was then poured onto an aluminum plate, where the residual solvent was slowly evaporated at 80 °C for 6 h and 120 °C for 2 h. After thermal imidization at 200 °C under vacuum for 48 h, crude brownish and transparent membranes with a thickness of between 150-200 μm in sodium salt form were obtained. The films were immersed in 1 N HCl aqueous solution for 2 days and soaked in deionized water for 1 day so as to obtain H⁺-form membranes. This water washing process was repeated three times. The membranes

with different IEC were prepared by changing the molar ratio of AESA-Na, BAPPDMS and APTES, as shown in Table 1. Since the product membrane has polyimide moiety, it is referred hereafter as poly(styrene-*co*-maleic imide), PSMI.

Characterization

FT-IR spectra were recorded on a Nicolet 5700 system in the range of 4000-450 cm^{-1} . Each sample was prepared by mixing with potassium bromide (KBr) pellets and then vacuum-dried at 80 °C to remove adsorbed water from the sample.

High-resolution solid-state NMR experiments were carried out on a Bruker AVANCE 400 spectrometer, equipped with a 7 mm double-resonance probe. The Larmor frequencies for ^{13}C and ^{29}Si nuclei are 100.58 and 79.46 MHz, respectively. Magic angle spinning (MAS) of the samples in the range of 5 kHz was employed for obtaining NMR spectra. The Hartmann-Hahn condition for $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization (CP) experiments was determined using adamantane, while proton decoupling was applied during acquisition to enhance the spectra sensitivity. Typically, a repetition time of 5 s was used in all NMR experiments. The ^{13}C and ^{29}Si chemical shifts were externally referenced to tetramethylsilane (TMS) at 0.0 ppm. A proton decoupling field strength of 60 kHz was used in all experiments.

The ion exchange capacity (IEC) was measured by classical titration. The membrane was soaked in a saturated NaCl solution, with released protons titrated using a 0.05 N NaOH aqueous solution.

For better accuracy, The IEC and water content of each sample were measured three times.

The reported values are based on averaged results.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Perkin-Elmer TGA 7) over a temperature range of 50-800 °C at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere.

The tensile property of the membranes was determined using Instron tensile testing machine equipped with an extensometer. Dumbbell-shaped specimens with a gauge length and a width of 10 and 4 mm, respectively, were stretched with a strain rate of 8.3×10⁻³ s⁻¹ at room temperature. Breaking stress was determined from the stress-strain curve.

Differential scanning calorimetry (DSC) measurement for dry membranes was conducted on a DuPont TA2010 analyzer at a heating rate of 20 °C min⁻¹ under a dry nitrogen atmosphere, and with an empty aluminum pan as a reference. Two types of water, freezing and nonfreezing water (bound water), in the fully-hydrated membranes were detected by melting transitions between -50 to +40 °C. The samples were first cooled from +25 to -50 °C, and then heated at a rate of 5 °C min⁻¹ up to +40 °C. Calculation of the amount of free water (ω_f) in the samples was completed by integrating transition heat capacity (ΔC_p) over the broad melting temperature interval in

$$\omega_f = \frac{\Delta H_m}{Q_{\text{melting}}} = \frac{\int \Delta C_p dT}{Q_{\text{melting}}}$$

where Q_{melting} is the heat of fusion of bulk ice (334 J g^{-1}). The weight fraction of bound water (ω_b) is calculated by subtracting the amount of freezing water (ω_f) from the total water uptake (ω_t). Then, the bound water degree ($\chi = \omega_b / \omega_t$) is obtained from the ratio of the amount of bound water to the total water uptake.

Proton conductivity of the polymer membranes was measured by an AC impedance technique using an electrochemical impedance analyzer (CH Instrument model 604A), where the AC frequency was scanned from 100 kHz to 10 Hz at a voltage amplitude of 10 mV. Fully hydrated membranes were sandwiched into a Teflon conductivity cell equipped with Au plates. The temperature dependence of proton conductivity was carried out by controlling the temperature from 30 to 95 °C at 95% RH.

Oxidative stability was examined by immersing the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm FeSO_4) at 80 °C for 1 h. The weight of the sample before and after Fenton test was recorded.

The cross-section morphology of the membranes was characterized by transmission electron microscopy (TEM) using JEOL JEM-1200CX-II microscope operating at 120 kV. The hybrid membranes were immersed in 1N Ag^+ aqueous solution overnight and rinsed with water for staining the hydrophilic domains. A 3 x 5 mm strip was cut from each membrane and dried under vacuum at 80 °C for 12 h. The samples were then sectioned to yield 50 nm

slices using an ultramicrotome, and picked up with 200-mesh copper grids for TEM observation.

The results of proton conductivity, DSC analysis and Fenton test have been carefully examined at least twice with membranes prepared in different batches. All data are reproducible with reasonable inaccuracy.

Single PEM electrolyzer test was evaluated using a unit cell with an active area of 1 cm^2 fed with a $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution with a rate of 2 ml min^{-1} by a peristaltic micropump. The membrane electrode assembly for the single cell test was fabricated as follows. Catalyst ink was prepared by mixing catalyst powder (E-TEK 20 % Pt/XC-72 for both anode and cathode) with water (2 ml for 1 g of electrocatalyst), and then adding isopropanol (20 ml for 1 g of electrocatalyst) to avoid any ignition. 5% Nafion dispersion (DuPont) was added (0.8 g solid Nafion for 1 g of catalyst) to the catalyst slurry. Catalyst coating on 30 wt% wet-proofing carbon paper (Toray TGP-H-120) with 1 cm^2 active area was fabricated by brushing Pt/C catalyst ink. The catalyst loadings on the anode and cathode layers were both 2 mg Pt cm^{-2} . The catalyst-coated GDLs were hot-pressed with the PSMI-3 membrane or Nafion-117 membrane (DuPont) at $140 \text{ }^\circ\text{C}$ under 30 kg cm^{-2} of pressure.

Table S1. Compositions, Ion exchange capacity, water uptake, proton conductivity and tensile strength of the composite ionomers.

Membrane	[-SO ₃ ⁻]:[BAPPDMS]: [APTES]: [TEOS]	IEC (meq g ⁻¹)	Water content(wt%	Conductivity ×10 ² (Scm ⁻¹) ^a	Tensile strength (MPa)
PSMI-0	0.50 : 0.33 : 0.17 : 0	1.06±0.09	36.6±0.4	2.7	33.3
PSMI-1	0.43 : 0.27 : 0.15 : 0.15	1.03±0.07	33.9±0.5	3.2	41.9
PSMI-2	0.48 : 0.26 : 0.13 : 0.13	1.22±0.12	43.8±0.7	4.8	38.3
PSMI-3	0.53 : 0.25 : 0.11 : 0.11	1.39±0.18	65.4±1.0	6.4	23.4
Nafion-117	---	0.91±0.10	20.6±0.4	4.1	23.0

^aMeasured at 90°C and 95 % R.H.

Table S2. States of water for the PSMI composite membranes and Nafion-117.

Membrane	Freezing water content, ω_f (wt%)	Bound water content, ω_b (wt%)	Bound water degree (%) ^a
PSMI-0	8.1	28.4	77.8
PSMI-1	5.1	28.8	85.0
PSMI-2	29.1	14.7	33.5
PSMI-3	35.6	14.5	29.0
Nnafion-117	6.7	13.9	67.5

^a ω_b/ω_t

Table S3. Oxidative stability of the PSMI composite membranes

Membrane	Loss (wt %)	Residue after test (wt %)
PSMI-0	18.5	81.5
PSMI-1	5.3	94.7
PSMI-2	10.7	89.3
PSMI-3	14.9	85.1
Nafion-117	1.1	98.9

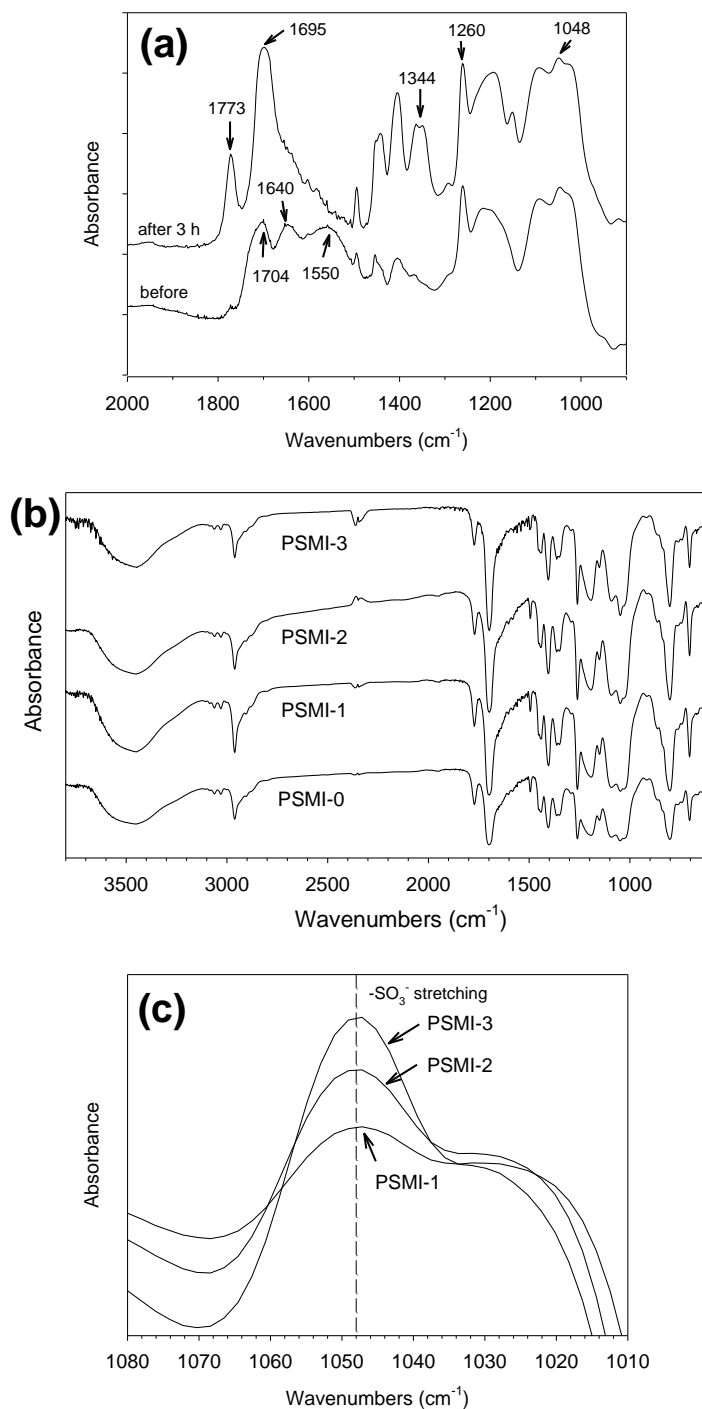


Fig. S1 FTIR spectra of (a) the PSMI-0 membrane before and after thermal imidation and (b) in the 600-3800 cm^{-1} region of the PSMI-0, PSMI-1, PSMI-2 and PSMI-3 membranes. (c) Detailed spectra in the 1010-1080 cm^{-1} region showing the $-\text{SO}_3^-$ stretching peak of the PSMI-1, PSMI-2 and PSMI-3 membranes.

The typical FTIR spectra in the 800 – 2000 cm^{-1} region of the membrane PSMI-1 before and after thermal imidization are shown in Fig. S1a. Before imidization, three absorption bands, at 1550, 1640 and 1700 cm^{-1} , show the valence oscillation of the C-NH, amide C=O, and COOH structures, respectively. The peaks at 1048 and 1260 cm^{-1} are respectively assigned to the $-\text{SO}_3^-$ symmetric and asymmetric stretching vibrations. [1] After thermal imidization at 200°C under vacuum for 3 hours, the first noticeable difference is the characteristic absorption bands of imide at 1344, 1705, and 1773 cm^{-1} , which are ascribed to C-N stretching of the imide ring, and symmetric and asymmetric imide carbonyl groups, respectively.[2] The absence of the amide peaks demonstrates the formation of an imide structure and the success of the side chain reaction. Fig. S1b compares the spectra in the 600 – 3800 cm^{-1} region of the PSMI-0, PSMI-1, PSMI-2 and PSMI-3 membranes. Fig. S1c shows the resolved spectra in the 1010 – 1080 cm^{-1} region of the PSMI-1, PSMI-2 and PSMI-3 membranes. The absorbance of these spectra was normalized by referring to the imide carbonyl peak at 1773 cm^{-1} . A progression in the relative intensity of the 1048 cm^{-1} band toward a higher absorbance indicates an increasing concentration of a sulfonate group for membranes PSMI-1 to PSMI-3.

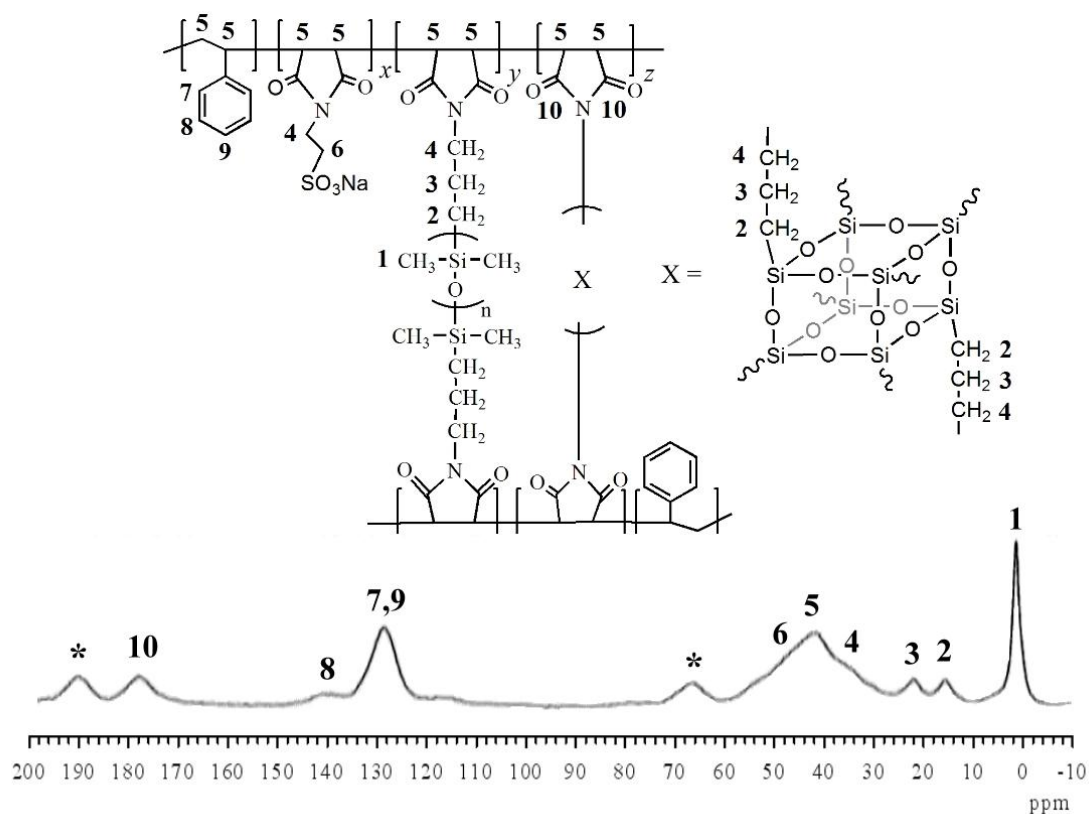


Fig. S2 ^{13}C CP/MAS NMR spectrum of the PSMI-1 membrane together with the assignments of the peaks.

Fig. S2 shows the typical ^{13}C CP/MAS NMR spectra of the PSMI-1 membrane. A sharp peak at $\delta = 2$ ppm is assigned to the methyl carbon on the silicon atom of BAPPDMS. The two peaks at $\delta = 16$ and 23 ppm are assigned to the methylene carbons in the α and β positions of the silicon atom, respectively. A broad signal, which ranged from 30 to 60 ppm, is composed of three superimposed peaks: the methylene carbon in the β and α positions at 36 and 53 ppm of the sulfonate group on the pendent AESA chain, and the methylene carbon on the polymer backbone at $\delta = 42$ ppm. The other downfield peaks at $\delta = 128$ and 180 ppm are ascribed to the aromatic carbon atom and carbonyl carbon of the imide ring.[3]

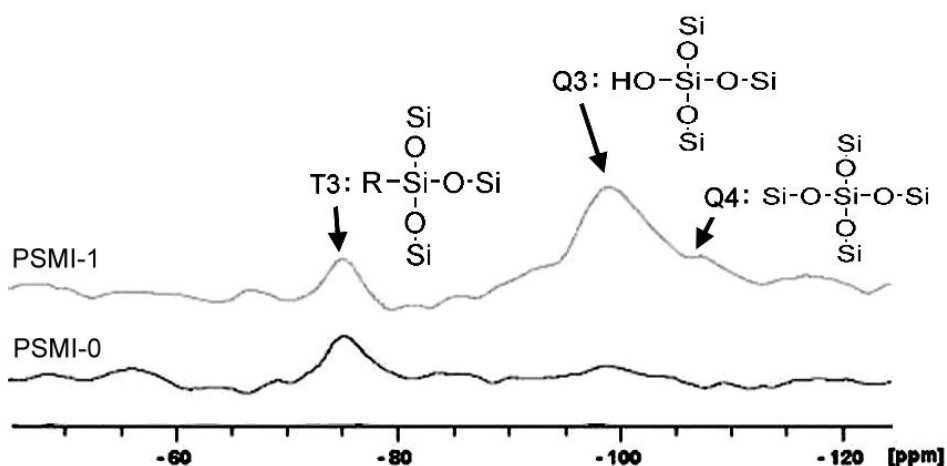


Fig. S3 ^{29}Si CP/MAS NMR spectra of the PSMI-0 and PSMI-1 membranes together with the assignments of the peaks.

The ^{29}Si NMR provides information about the levels of condensation and the structure of the inorganic network of the hybrid materials. Fig. S3 shows the typical ^{29}Si CP/MAS NMR spectra of the PSMI-0 and PSMI-1 membranes, together with the assignment of T^3 -, Q^3 - and Q^4 -group of silicon. The signal at $\delta = -75$ ppm of the PSMI-0 is attributed to the condensed siloxane fragments in T^3 [RSi(OSi)_3] which indicates a predominating degree of the three-dimensional silsesquioxane in the hybrid membrane. As for PSMI-1, the presence of major signal of Q^3 [Si(OH)(OSi)_3] at $\delta = -100$ ppm and the minor peak of Q^4 [Si(OSi)_4] at $\delta = -107$ ppm can be referred to the POSS structure.[4]

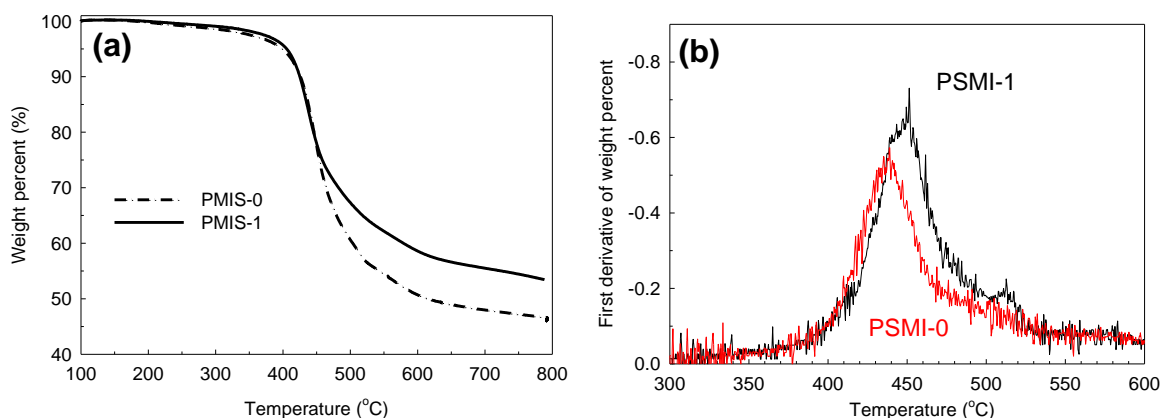


Fig. S4 (a) TGA thermograms and (b) the first derivative profiles of PSMI-0 and PSMI-1 membranes under N₂.

The PSMI-0 and PSMI-1 ionomers were subjected to thermogravimetric analysis (TGA) to evaluate the effect of POSS on their thermal property. The TGA thermograms of the hybrid ionomers (Fig. S4a) showed a weight change at around 400~500 °C, which corresponds to the thermal degradation temperature of the poly(maleic imide-*co*-styrene) main chain. The maximum thermal decomposition temperature T_d is determined by the first derivative of weight change as shown in Fig. 4b. It can be observed that the T_d of PSMI-0 (439 °C) is slightly lower than that of the PSMI-1 (452 °C), indicating the reinforcement by the POSS moieties.

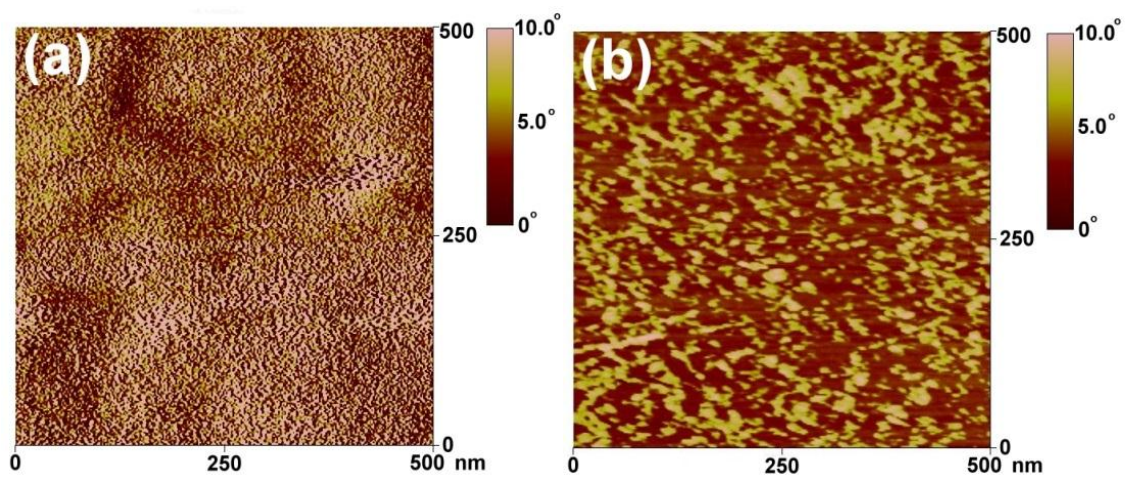


Fig. S5 AFM phase images of (a) the PSMI-1 and (b) the Nation-117 membrane with a scan size of 500 nm \times 500 nm.

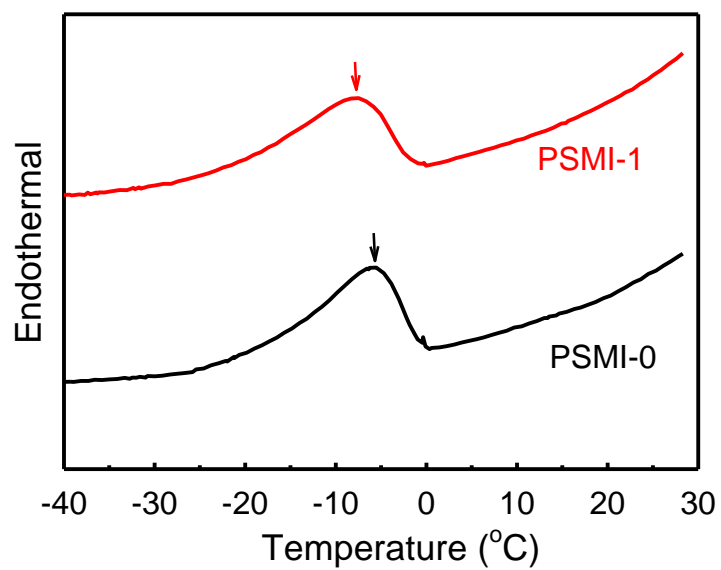


Fig. S6 DSC thermograms of the fully hydrated PSMI-0 and PSMI-1 membranes in the -40 to 30 °C range.

References:

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