Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Free Volume, Gas Permeation, and Proton Conductivity in MIL-101-SO_3H/Nafion Composite Membranes

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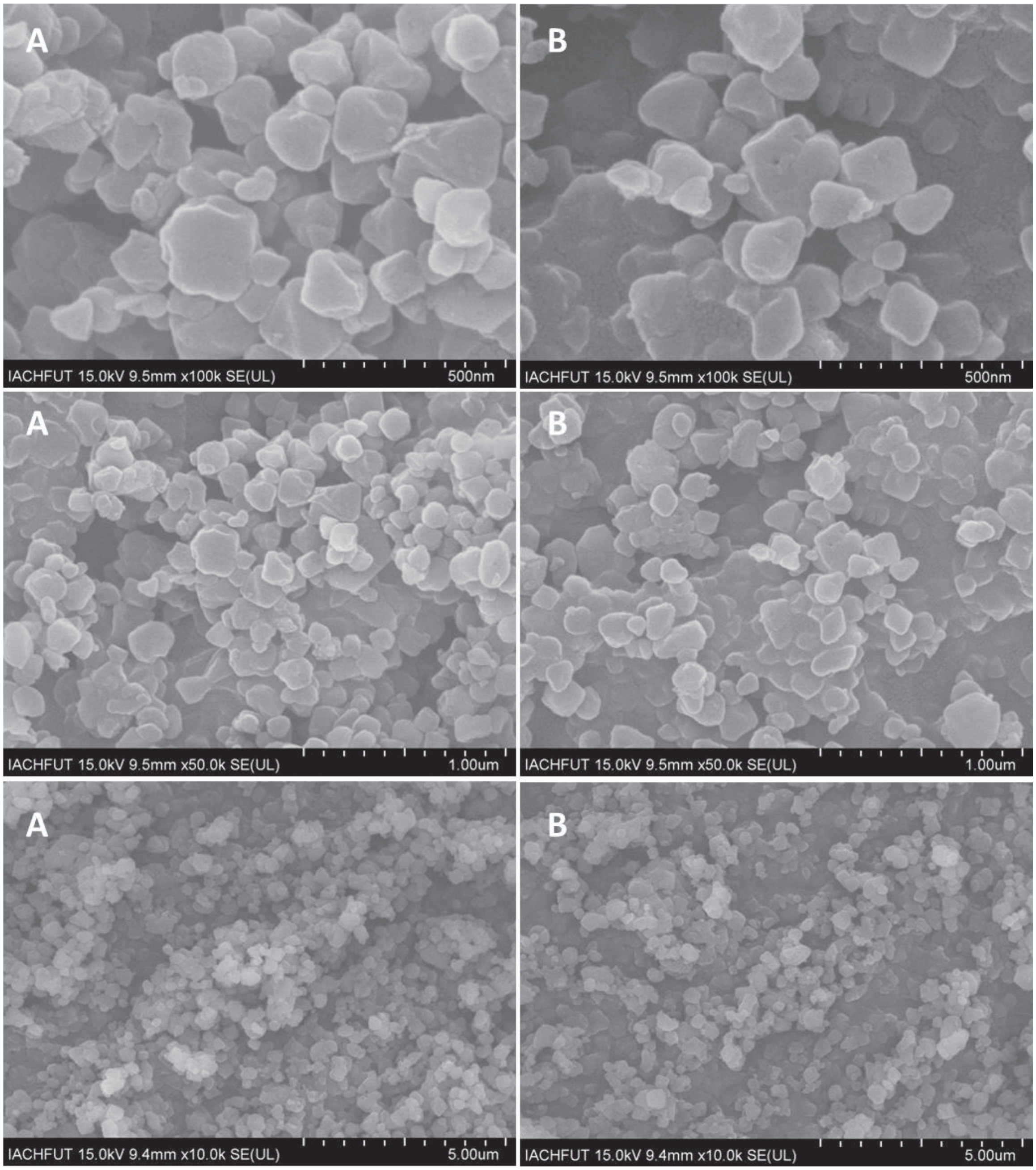

Fig. S 1 SEM images of (A) the MIL-101 and (B) the MIL-101-SO_3H particles.

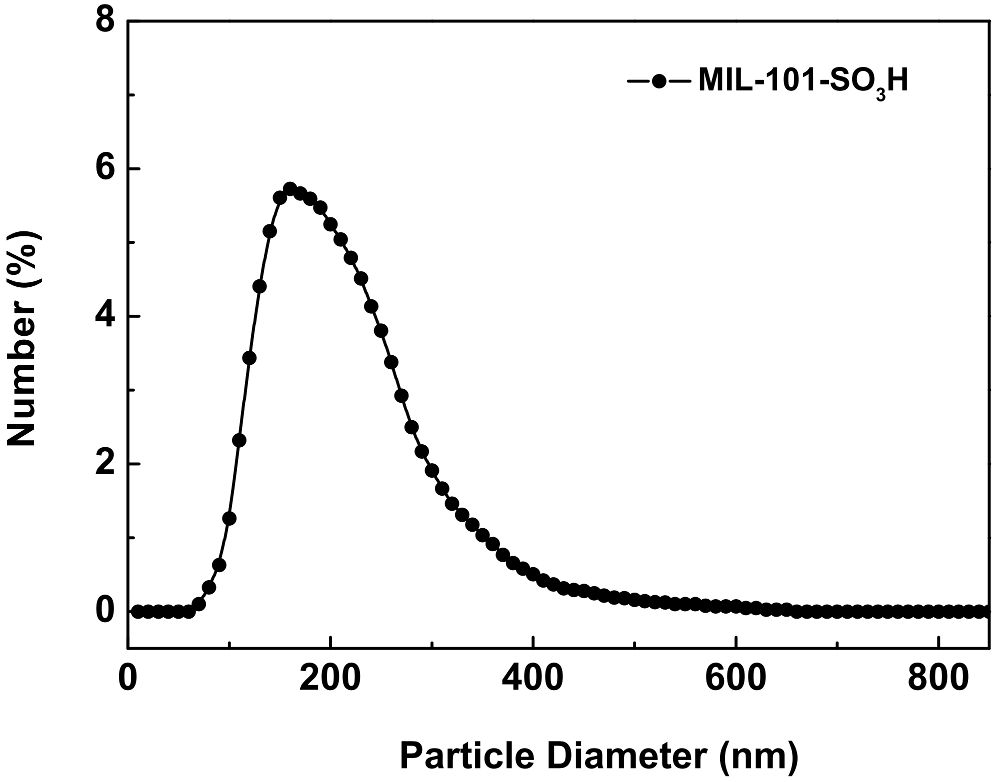

Fig. S 2 Particle-size distribution of the MIL-101-SO$_3$H particles.

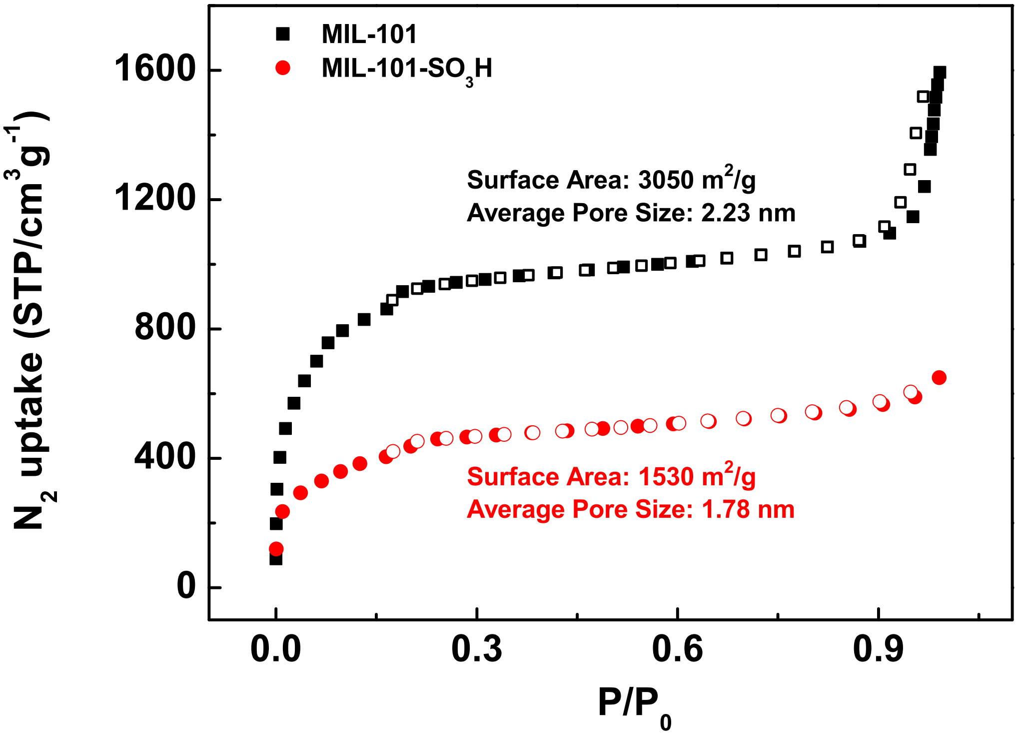

Fig. S 3 N_2 adsorption (solid) - desorption (void) isotherms of the MIL-101 (square) and the MIL-101-SO_3H (circle) particles.

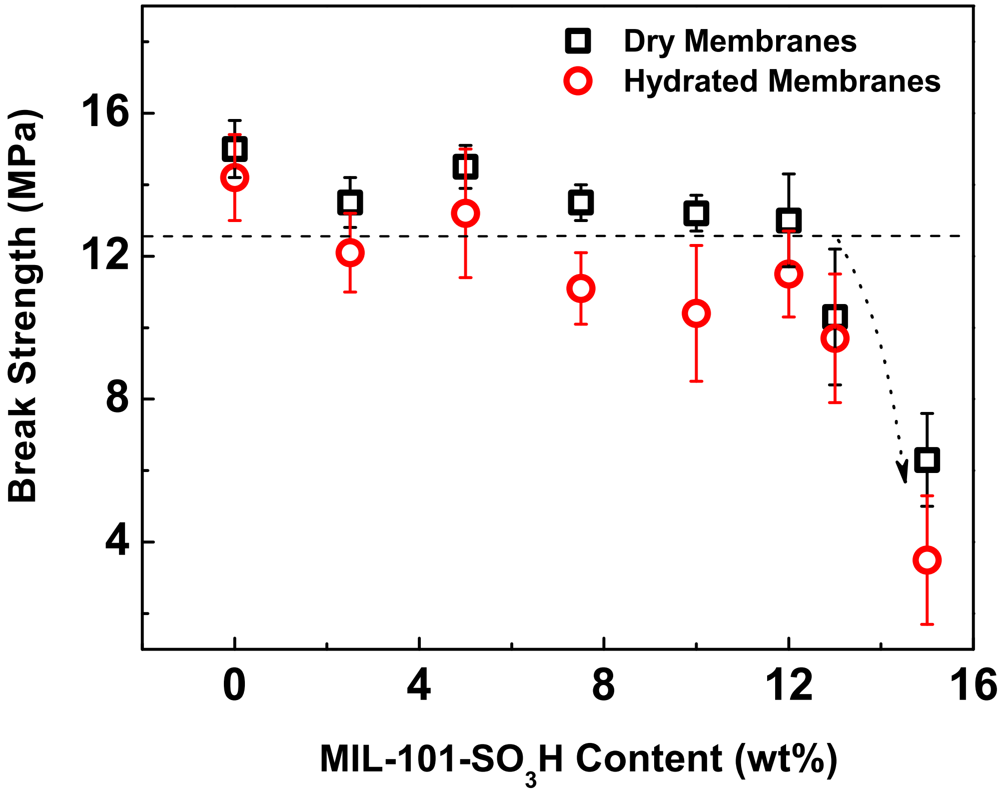

Fig. S 4 Break strength of MIL-101-SO_3H/Nafion composite membranes as a function of MIL-101-SO_3H content, dashed line and dashed arrow are guides to the eyes.

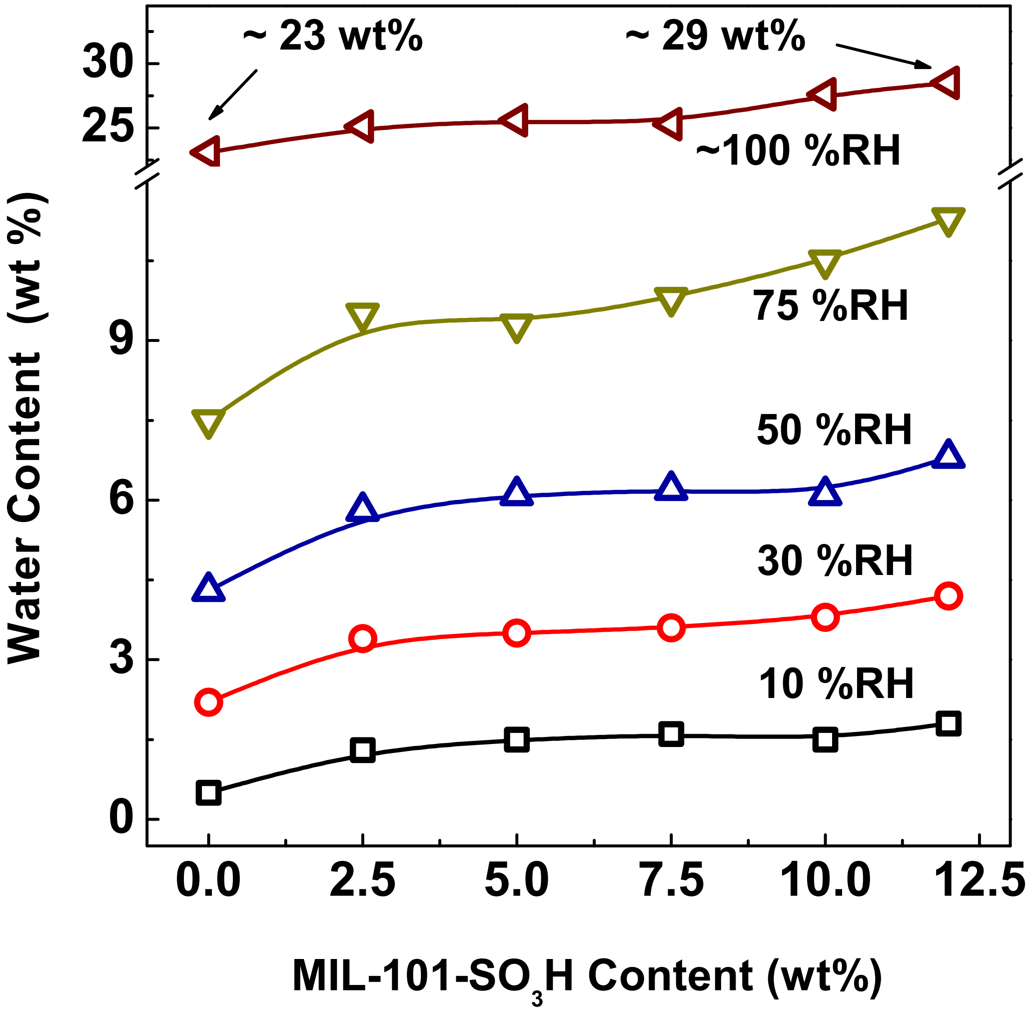

Fig. S 5 Water uptake of MIL-101-SO_3H/Nafion composite membranes as a function of ambient humidity, at room temperature.

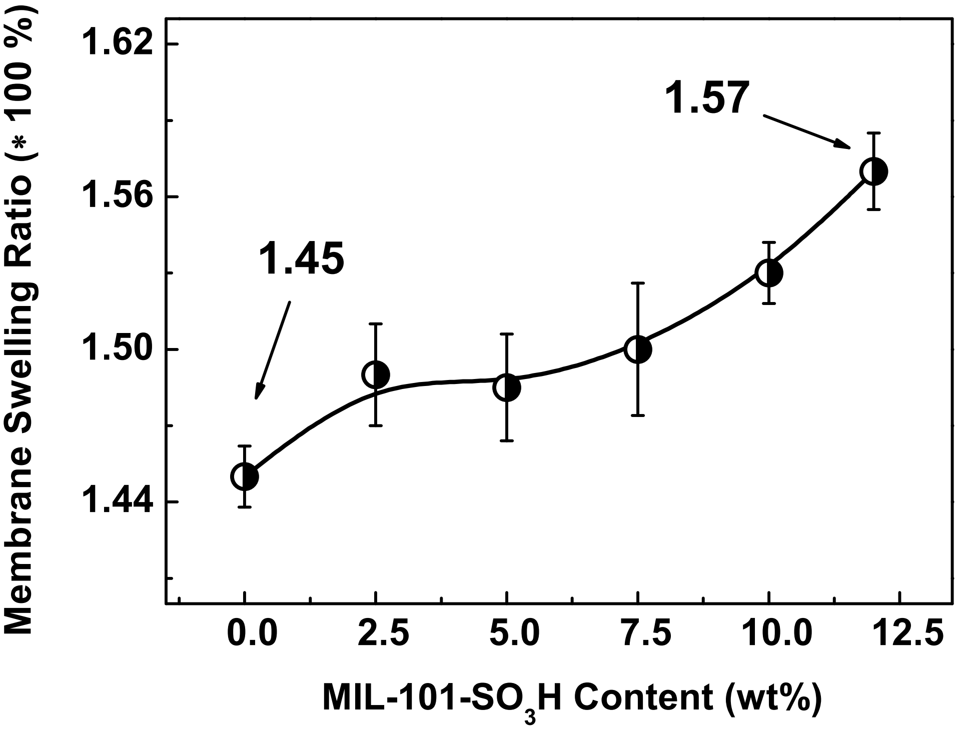

Fig. S 6 Swelling behavior of MIL-101-SO_3H/Nafion composite membranes, at room temperature.

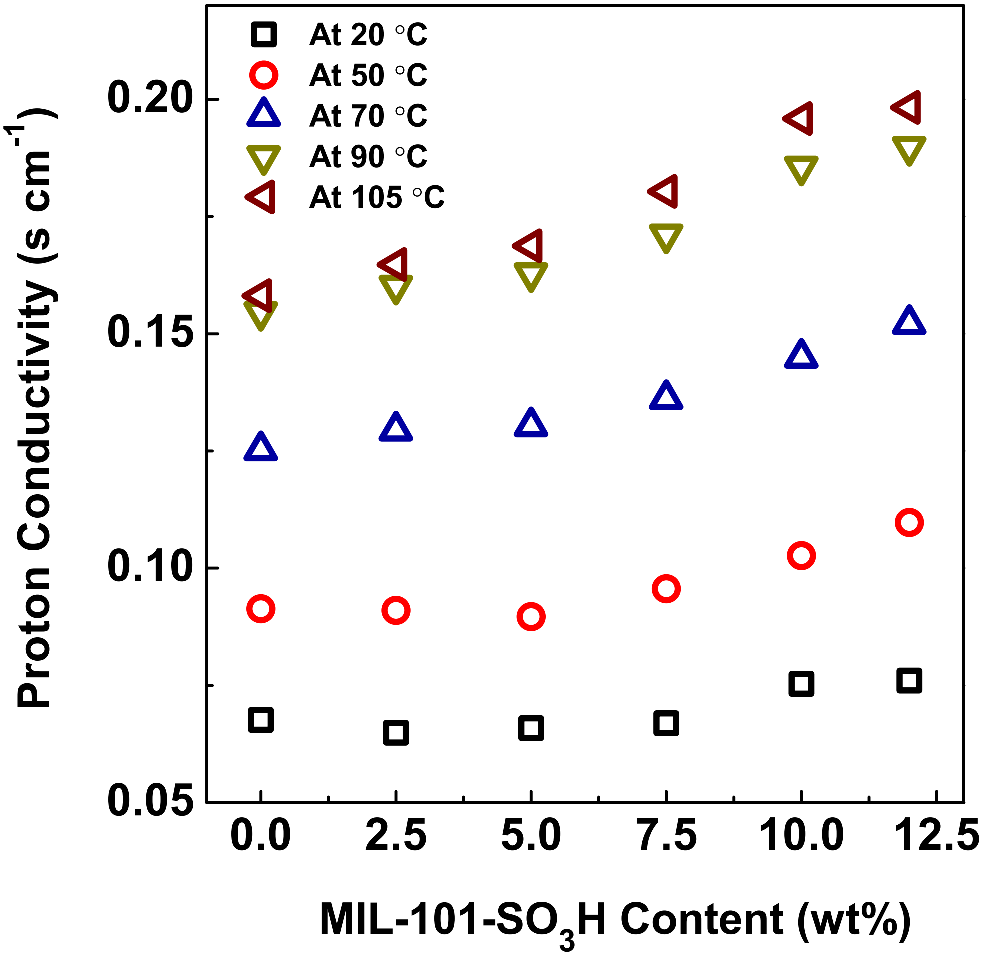

Fig. S 7 Proton conductivity of the composite membranes as a function of MIL-101-SO_3H content.

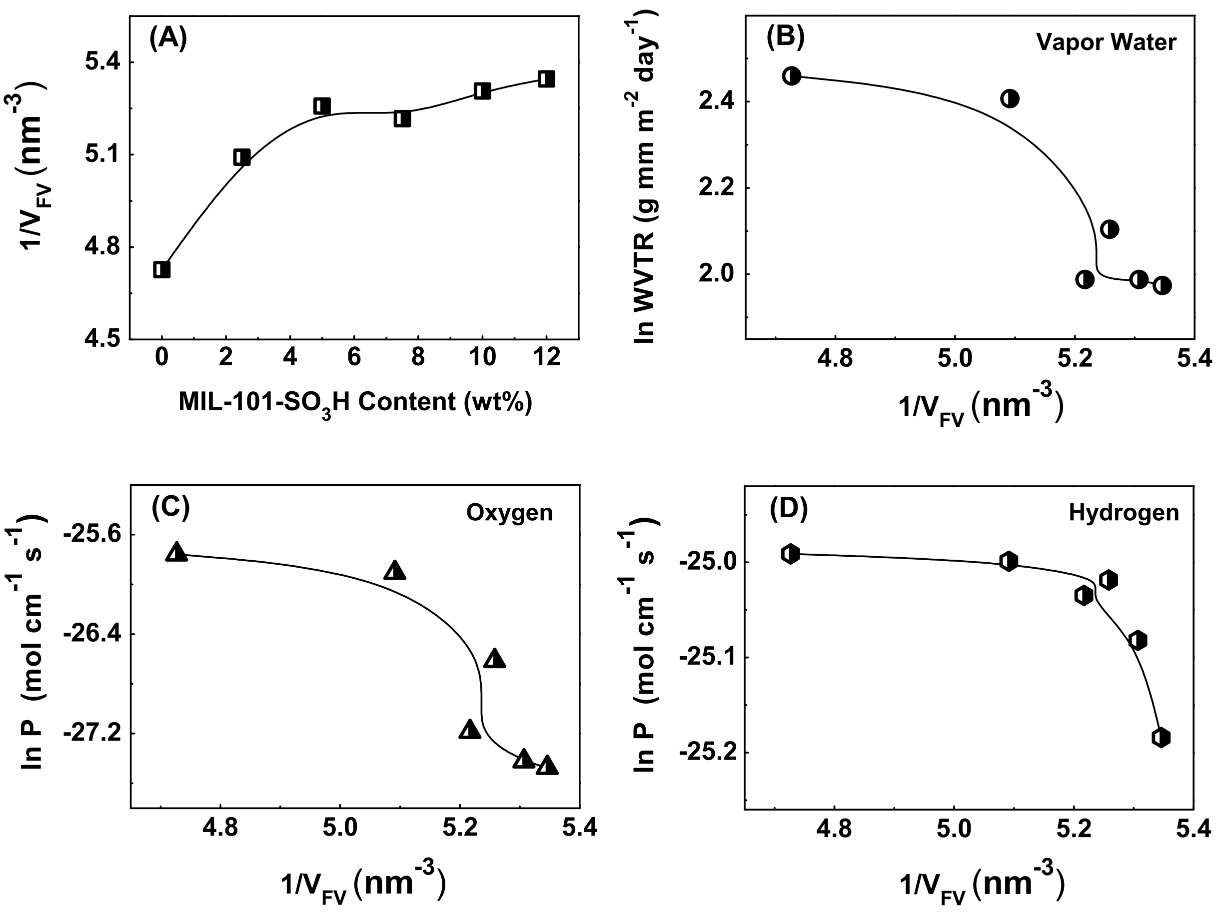

Fig. S 8 (A) The reciprocal value of V_{FV} in MIL-101-SO_3H/Nafion composite membranes and the plots of logarithmic (B) WVTR, (C) oxygen permeability, and (D) hydrogen permeability versus reciprocal V_{FV}.

Materials

Solution of Nafion (DuPont, DE-520, EW 1100, 5 wt% of perfluorosulfonate resin (H^+ form) and 95 wt% of isopropanol/water mixture) was used to prepare the membranes. Deionized water (purified with Milipore, resistivity= 18 MΩ cm^{-1}) were used in this work. All other solvents and chemicals were reagent grade and were used as received. Before measurements, membranes were cleaned through a standard procedure: (1) being boiled in 5 % H_2O_2 solution for 0.5 hour; (2) being rinsed in boiling deionized water for 0.5 h; (3) being boiled in 0.5 M H_2SO_4 solution for 0.5 hour; (4) finally being rinsed again in deionized water.

MIL-101 particles were synthesized by a hydrothermal reaction of terephthalic acid (1 mmol) with $Cr(NO_3)_3{\cdot}9H_2O$ (1 mmol), HF (0.5 mmol), and H_2O (265 mmol) at 220 °C for 8 h. Boiling water at 70 °C for 5 h and hot ethanol at 60 °C for 3 h were used to wash and purify the MIL-101, until no detection of colored impurities in the mother liquor solution. Then, to further purify the MIL-101, MIL-101 was dispersed in 150 mL of an aqueous solution of 30 mM NH_4F at 60 °C for 10 h. Finally, MIL-101 was filtered and washed thoroughly with hot water.[1,2] These reactions produced a crystallized green powder of MIL-101.

FTIR, mechanical property, SEM, XRD, XRPD, BET and particle size distribution measurements

FTIR was used to determine surface chemical bonding and structure of the MIL-101 and MIL-101-SO_3H particles. Before the measurements, samples were mixed with the dry KBr powder and were mechanically pressed to discs. FTIR was carried out at room temperature at a resolution of 2 cm^{-1} by a Nicolet 170 SXIR spectrometer in the range of 4000 cm^{-1} to 500 cm^{-1}. The mechanical properties of prepared membranes were measured on a tensile machine (HDV, HANDPI) at room temperature (∼20 °C) and room humidity (∼50 RH%). Dumbbell type specimens were placed between the grip of the testing machine, and deformed under tension at a tensile rate of 2 mm min^{-1} at room temperature. The side length and thickness of the membrane specimens (taken as the average of three measurements distributed over the sample) were 40 mm and 50±10 μm, respectively. Three specimens were tested for each membrane. The morphologies of MIL-101 and MIL-101-SO_3H were measured by SEM (NJL-120A, Novel Optics). The XRD and XRPD measurements were performed on a D8 ADVANCE type diffractometer under ambient condition (20 °C and 50 %RH), and the scan rate was 4°/ min^{-1}. Before the measurement, all samples were completely dried in a vacuum at 60 °C, and then they were separately sealed in the sealing bags until conducting the measurement. The porosity of the samples was characterized by N_2 adsorption-desorption (JW-BK 122W, JWGB, China) at 77 K. The particle size distribution of MIL-101-SO_3H was analyzed by a laser particle analyzer (Mastersizer 3000, Malvern, Britain).

Water uptake and swelling ratio measurements

Prior to the water uptake measurements, the obtained membranes were completely dried in a vacuum at 60 °C, weighted and immersed in de-ionized water for 48 hours. Subsequently, the saturated membranes were re-weighted after carefully removing the surface-adsorbed water by tissue paper. Water uptake tests were conducted three times for each membrane, and the results are presented by the mean values. Water uptake was calculated as follows,

$$Water \quad Uptake(\%) = 100 \times \frac{(M_{wet} - M_{dry})}{M_{dry}} \quad , \tag{1}$$

where M_{wet} and M_{dry} are the weights of saturated and dried Nafion membranes.

The geometrical expansion (swelling ratio) of Nafion membranes was calculated from the variation in volumes of dry (V_{dry}) and water saturated (V_{wet}) Nafion membranes. Thickness of membranes was measured by a micrometer screw gauge with a resolution of 1.0 μm, and was reported as an average of three measurement points for each strip-shaped membrane. Length and width of membranes were measured with a vernier caliper of 0.02 mm resolution. Swelling behavior were conducted three times for each membrane at 25 °C, and the mean values were presented as the final results.

Proton conductivity measurements

Proton conductivities of the membranes were measured by an AC impedance technique in the frequency range of 1 Hz and 100 kHz, to measure in-plane bulk conductivity of membranes. The measurements were conducted on an electrochemical workstation (CS350H, Corrtest, China) with a signal amplitude of 10 mV at the open circuit condition. The as-prepared membranes (2 cm × 4 cm) were stuck on the electrodes of two platinum sheets, whose distance was 2 cm. Then the two platinum electrodes together with the membrane sample were sandwiched between two polysulfone sheets. The details of the measurements set up can be found in the literature.[3] Proton conductivity (σ) was determined by AC impedance (R) along with the distance between the electrodes (L), width (W) and thickness (T) of the membrane using the following equation,

$$\sigma = \frac{L}{R \times W \times T}. \tag{2}$$

Proton conductivities of membranes at various temperatures were evaluated in a testing chamber with controllable temperature ranging from 25 °C to 140 °C, and all membranes were fully hydrated before measurements. During the measurement, the sample cell was closed and without external humidification.

Positron annihilation lifetime measurements

The positron annihilation experiments were conducted by using a fast-fast coincidence PALS with a time resolution function of 0.230 ns for the full width at half maximum (FWHM), and 1 million counts were collected for each spectrum. A ^{22}Na source ($\sim$10 μCi) was firstly sandwiched by $\sim$20 pieces of samples (membranes, or MIL-101-SO$_3$H and MIL-101 tablets prepared with direct compression method) and then covered with an Al foil. PALS measurement was conducted under room temperature (25 °C) and room humidity ($\sim$80 %RH) for membranes, and under vacuum for MIL-101-SO$_3$H and MIL-101 tablets. The PATFIT program[4] as well as the LT program[5] were applied to analyse the positron lifetime spectra of the membranes, and the variances of the fits were in the range of 0.96$\sim$1.10. Details of PALS measurements set up can be found in our recent paper.[3] The average radii of free volumes are derived from the τ_{o-Ps} according to a spherical approximation given by the Tao-Eldrup model as,[6,7]

$$\tau_{o-Ps} = 0.5[1 - \frac{R}{R_0} + \frac{1}{2\pi} sin(\frac{2\pi R}{R_0})]^{-1}(ns) \tag{3}$$

where R_0=R+ΔR, and ΔR=0.166 nm is the thickness of the o-Ps wave function overlapping with the homogeneous electron layer. Application of positron annihilation lifetime spectroscopy (PALS) to polymer membranes relies on the fact that a part of the injected positrons combine with electrons from surrounding molecules to form positronium (Ps) atoms in them. Ps is a hydrogen-like bound state of a positron and an electron with two spin states: spin antiparallel para-positronium (p-Ps) and spin parallel ortho-positronium (o-Ps). These three annihilation branches of positrons can be respectively characterized by their lifetimes τ_1 ($\sim$125 ps), τ_2 ($\sim$300 ps), τ_3 (1$\sim$10 ns) and the corresponding relative intensities. Being the longest lived component, the o-Ps lifetime (τ_{o-Ps}) is of particular importance for the studies of polymer free volumes because it is related to the average free volume hole size and it is determined by the overlapping of positronium wave function with that of the electrons on the wall of free volume holes in the polymer.[6–9]

Water vapor transmission rate (WVTR) and gas (hydrogen and oxygen) permeability measurement

A cup method was used to obtain the WVTR of membranes.[10] Firstly, fill a cup (made of hard plastics) with a certain amount of anhydrous calcium chloride ($CaCl_2$), and seal the cup with a tested membrane. Then, keep the cup under a constant environment condition (80% relative humidity and 25 °C), measuring and recording the mass of cup over a period of time. WVTR is defined as the Equation as shown below,

$$WVTR = \frac{\Delta m \cdot d}{A \cdot t} \tag{4}$$

where Δm is the mass difference between two consecutive measurements within a time of t, d is the thickness of the membrane, A is the effective area of the membrane used for water vapor transmission, and t is the time interval between two consecutive measurements.

Gas (Hydrogen and Oxygen) permeability was measured by a differential pressure method on a Labthink VAC-V2 apparatus, monitoring the amounts of O_2 and H_2 that permeated across the membrane from one side to the other, under a constant environment condition (80% relative humidity and 25 °C). The operating pressure difference is 1 atm.

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