

Supplementary Data

Poly(vinylidene fluoride-co-hexafluoro propylene) nanohybrid membrane using swift heavy ions irradiation for fuel cell application

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Detailed experimental procedure

Gas Permeation tests: Three parallel cells method have been used for the gas permeabilities of pure *HFP* and its nanohybrid membrane using pure nitrogen (N₂) gas under constant pressure. A circular 0.785 cm² area and 0.03 mm thickness membrane sample was placed in the cell and the sealing was made using aluminum foils and glue. Feed pressure was set at 80 psi and the other side was maintained at atmospheric pressure. Soap bubble flow meter was used for determining the gas permeation rate. Every experiment was carried out three times for reproducibility and the average of the results was reported. The gas permeability was determined from the following eqn:

$$\text{Gas flow rate (Gfr)} = \frac{10 \text{ ml}}{t_{\min} \times 60} \quad (1)$$

where, t_{\min} is the time (sec) of gas flow of the permeate gas passing through the membrane (cm³/s). Gas flux was calculated from the Gfr per unit area where, gauge pressure was considered as 80-14.69 psi. Gauge pressure indicates the complete pressures difference of the feed side and the permeate side (cmHg). Then, the normalized gas flux was calculated using the eqn:

$$\text{Normalized gas flux (NGF)} = \frac{\text{Gas flux}}{\text{Guage pressure}} \quad (2)$$

and, gas permeability coefficient (GPC) = NGF × membrane thickness, where, permeability was expressed in barrer (1 barrer = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹).

Electrical characterization: The dc conductivity (σ) was assessed by typical spring loaded pressure contact two-probe technique using a pico-ammeter (*Model: DPM-111*) for current (I) was measured after passing a constant voltage (V) across the sample from a high voltage power supply (*Model: EHT-11*). A circular smooth film of 0.845 cm diameter coated with *Ag*-paste, for better contact, was used for the measurement. The resistivity (ρ) was calculated from the equation below;

$$\rho = \frac{R \times A}{l} \quad (3)$$

where, ρ = resistivity (Ω cm), R = resistance (Ω), A = surface area (cm²) and l = thickness (cm) and the conductivity (σ) was calculated using the relation $\sigma = 1/\rho$. Same experiment was conducted thrice and the average was taken as the conductivity of the samples. Temperature dependent conductivity was measured in a broad range of temperature from 25 to 125 °C. The activation energy (E_a) was calculated from Arrhenius equation as mentioned below;

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{RT} \quad (4)$$

where, σ is the conductivity of the samples (S.cm⁻¹), σ_0 , pre-exponential factor (S.K⁻¹.cm⁻¹), E_a , activation energy of conduction (kJ.mol⁻¹) governed by the Grotthuss type mechanism, R , ideal gas constant and T , temperature (K). The current-voltage (I-V)

characteristics of the films were measured by using the sample from -10 to +10 V at room temperature using STM mode attached with AFM.

Proton conductivity measurement: Membrane conductivity measurements were performed using ac impedance spectroscopy in humidified condition via a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30). The membrane samples were sandwiched between two domestic made stainless steel circular electrodes (4.0 cm²). Sinusoidal alternating current with frequency range of 1 to 10⁶ Hz and 1 μA/s scanning rate was applied to the electrodes. The spectrum of the blank short-circuited cell was also collected and this data was subtracted (as a series circuit) from each of the recorded spectra of the membranes to remove cell and inductances and wiring resistances. The corrected spectra were viewed as complex impedance plots with the real component of Z' on the X-axis and imaginary component of Z'' on the Y-axis ($Z = Z' - iZ''$); the ionic resistance of each membrane was predictable to be the crossroads of the X-axis with the extrapolation to the low frequency. The membrane resistance was determined from Nyquist plots using the Fit and Simulation method. The proton conductivity (κ^m) of each membrane was calculated from eqn. 5:

$$\kappa^m(S/cm) = \frac{L(cm)}{[R(\Omega) \times A(cm^2)]} \quad (5)$$

where, L is the distance between the electrodes used to measure the potential, R is the resistance of the membrane and A is the surface area of the membrane.

Methanol permeability: Methanol permeability of the functionalized membranes was measured in a diaphragm diffusion cell, consisting of two compartments with a capacity

of approximately (80 cm³), separated by a vertical membrane with 20 cm² effective area. The membrane was compressed between two compartments, which were stirred throughout the experiments. Before the experiment, membranes were equilibrated in water-methanol mixture for 12 h. Initially, one compartment (A) contained 30% methanol-water mixtures while other (B) contained double distilled water. Methanol flux across the membrane aroused due to concentration gradient. Methanol concentration in compartment B with respect to time was observed by measuring the refractive index with digital refractometer (Mettler Toledo RE40D). The methanol permeability (P) was obtained by the equation given below:

$$P = \frac{1}{A} \frac{C_{B(t)}}{C_A(t - t_0)} V_B L \quad (6)$$

where, A is the effective membrane area, L the thickness of the membrane, $C_{B(t)}$ the methanol concentration in compartment B at time t , $C_A(t - t_0)$ is the change in the methanol concentration in compartment A between time 0 and t , and V_B the volume of compartment B. All experiments were carried out at 30 °C. Uncertainty for each measurement was less than 2%.

Preparation of membrane electrode assembly (MEA): MEA was fabricated by previous reported technique and consists of three-layer structure (AM, anode/cathode catalyst layer and diffusion layers). The carbon paper (Toray Carbon Paper, thickness: 0.27 mm) was wet proofed with 12 wt.% PTFE solution using brush painting method. The gas diffusion layer (GDL (25 cm² geometric area) was fabricated by coating slurry of carbon black (Vulcan XC72R) (0.95 mg/cm²) containing PTFE dispersion on carbon paper. The

anode was made by coating a slurry of catalyst (20 wt% Pt+10 wt% Ru on carbon) and Nafion ionomer (5 wt%) solution in mixture of isopropanol and Millipore water (catalyst ink). Loading of Pt and Ru in GDL was 1 mg and 0.5 mg, respectively. While the cathode acquired by coating, the same catalyst ink lacked Ru with similar loading. Electrodes were cold pressed membrane followed by curing at 60 °C for 12 h and then hot pressed at 130 °C for 3 min at 1.2 MPa. The MEA was clamped in single cell (FC25-01 DM fuel cell). The current–voltage polarization curves were recorded with the help of MTS-150 manual fuel cell test station (ElectroChemInc., USA) with controlled fuel flow, pressure and temperature regulation attached with electronic load control ECL-150 (ElectroChem Inc., USA). The measurements were performed in the air mode of operation at 10 psi pressure with 30% MeOH-water mixture at the anode side with pressure 7 psi at 70 °C for a representative membrane.

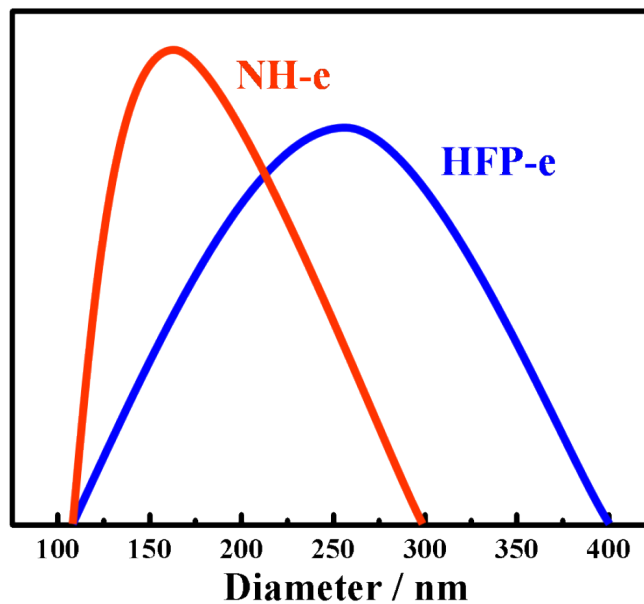


Figure S1: AFM topographs of allocation of nano-channel diameter of the irradiated etched *HFP-e* and *NH-e* at a fluence of 5×10^{10} ion/cm² as shown in *Fig. 1c* of the manuscript.

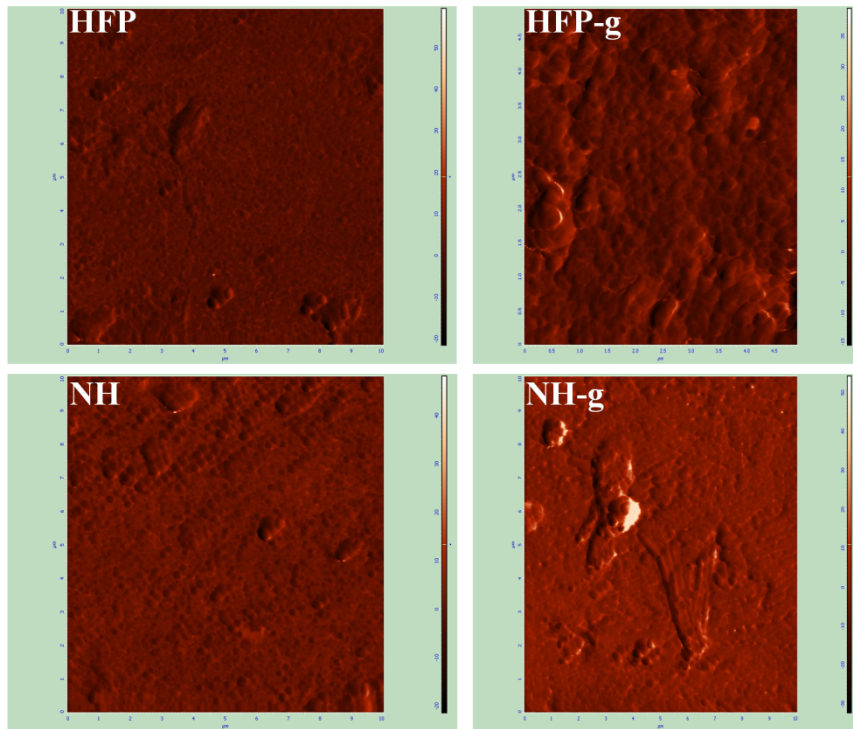


Figure S2: AFM topographs of neat *HFP*, *HFP* after 3HT grafting (*HFP-g*), neat *NH* and *NH* after 3HT grafting (*NH-g*) with fluence 5×10^{10} ions/cm². It should be also mentioned that after 3HT grafting on both *HFP* analogous *NH* do not display any channel.

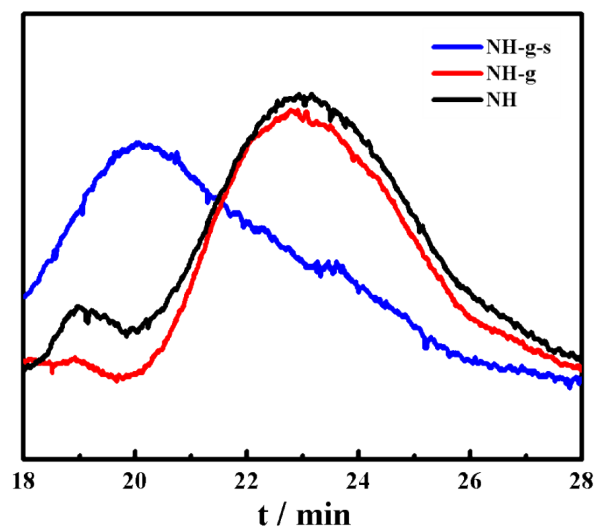


Figure S3 GPC traces of neat *NH*, *NH-g* and grafted sulphonated *NH-g* specimens.

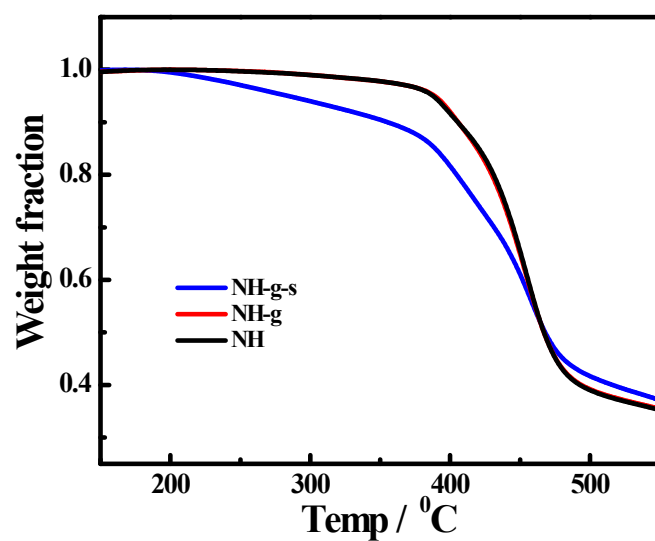


Figure S4: TGA thermograms of neat *NH*, *NH-g* and *NH-g-s* with fluence 5×10^{10}

ions/cm².

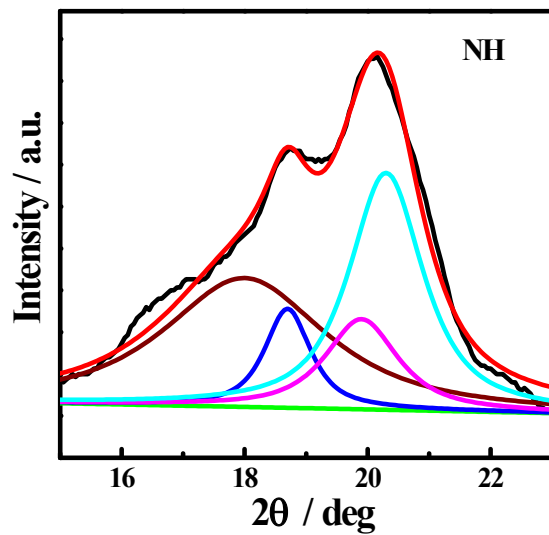


Figure S5: Deconvolution of pure NH larger peak area equivalent to β -phase and the broad is the amorphous peak.

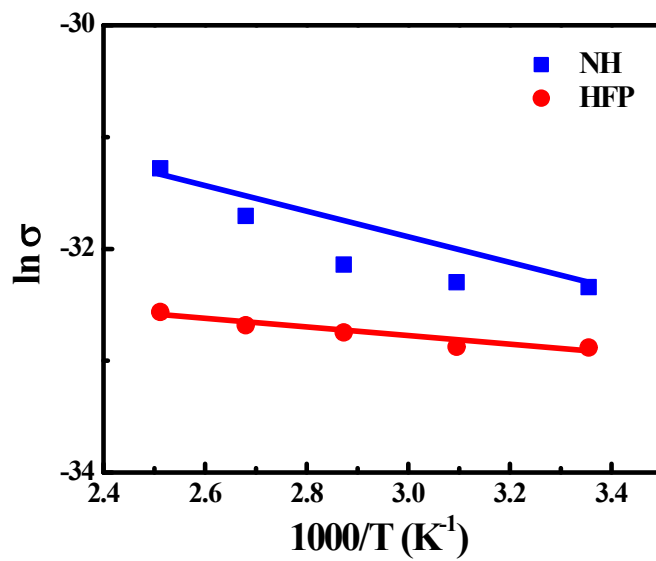


Figure S6: Comparison of electrical conductivity as a function of temperature ($1000/T$) of pristine *HFP* and *NH*.