

Supporting Information

***N*-o-sulphonic acid benzyl chitosan (NSBC) and *N,N*-dimethylene phosphonic acid propylsilane graphene oxide (NMPSGO) based multi-functional polymer electrolyte membrane with enhanced water retention and conductivity**

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S1. Instrumentation

Infrared spectra of APSGO, NMPSGO, were recorded by KBr technique in the range of 4000-400 cm⁻¹ while for dried membrane (NSBC/NMPSGO-8) by ATR technique with spectrum GX series 49387 spectrometer in the range of 4000-700 cm⁻¹. Solid state ³¹P NMR spectra of dried membrane (NSBC/NMPSGO-8) (grind the membrane in liquid nitrogen) were recorded by using spectrometer (Bruker 500 MHz). Wide angle X-ray diffractograms (WXRDS) were recorded using a Philips Xpert X-ray diffractometer with Cu-Kα (1.54056) radiation.

Transmission electronic microscopy (TEM) images of the APSGO and NMPSGO samples were recorded using a JEOL JEM 2100 microscope. The powder samples were dispersed in ethanol and mounted on a lacey carbon Formvar coated Cu grid. Cross-section image of the composite membrane was analyzed by Scanning electron microscopy (SEM) using a Leo microscope (Kowloon, Hong Kong) after gold sputter coatings on samples. Optical images of different membranes were taken by Nikon digital camera (D5100 AF-S DX NIKKOR 18-55mm f/3.5-5.6G VR).

Thermo gravimetric analyzer (NETZSCH TG 209F1 Libra TGA209F1D-0105-L) were used for the investigation of thermal stability of the membranes under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 800 °C. The mechanical stability of membranes were

analyzed by heating the sample from 0 to 350 °C under nitrogen atmosphere with 10 °C/min heating rates using NETZSCH DMA 242 instrument. Burst strength tester machine provided by Test Techno Consultant, Vadodara, Gujarat, India (Model 807 DMP), was used for the investigation of pressure (Kg cm⁻²) required to rupture the membrane.

S2. Water Uptake and Swelling Ratio

The water uptake was determined by taking the constant weight of dried membrane and weight of wet membrane after immersed membrane in distilled water for 24 h at room temperature. The water uptake was calculated from the equation:

$$\text{Water uptake (wt \%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where W_{wet} and W_{dry} are the weight of wet and dry membrane respectively.

Swelling ratio of the membrane was measured by immersed the membrane in water at 65 °C for 12h using the equation (2):

$$SW\% = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \quad (2)$$

where L_{wet} and L_{dry} may be the length/width/thickness of the swollen and dry membrane respectively.

Number of water molecules associated per ionic sites (λ) was calculated according to the following relationship:

$$\lambda = \frac{\text{water uptake}(\%)}{IEC \times MW_{H_2O}} \quad (3)$$

where MW_{H_2O} is the molecular weight of water.

S3. Ion Exchange Capacity (IEC)

The ion exchange capacity (IEC) of the membranes was measured by the back-titration technique. The 1 cm² piece of dry samples were soaked in 100 ml of 1M NaCl solution for 24h to replace the all H⁺ ions of membrane to Na⁺ ions. The exchanged H⁺ was back titrated with a 0.005 M NaOH aqueous solution using phenolphthalein as an indicator. The IEC value (in mequi/g) is obtained from following equation:

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad (4)$$

where V_{NaOH} is the volume of NaOH solution, C_{NaOH} is the concentration of the NaOH solution and W_{dry} is the weight of dry membrane.

S4. Stability Testing

The oxidative stability of prepared membranes was examined by dipping the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 3 ppm $FeSO_4$) at 80 °C for 1 h. For hydrolytic stability test, a small piece of membrane was kept in a pressurized closed vial containing distilled water for 24 h at 140 °C. The stability was evaluated by observing the loss in weight, IEC and conductivity after treatment.

S5. Proton Conductivity of Composite Membranes

Proton conductivity of composite membranes was measured by using a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30). The membranes were mounted between two in-house made stainless steel circular electrodes (4.0 cm^2), which were then placed in DI water. Direct current (DC) and sinusoidal alternating currents (AC) were supplied to the respective electrodes for recording the frequency at $1\text{ }\mu\text{A/s}$ scanning rate within 10^6 to 1 Hz. Using Fit and Simulation method resistance were measured from Nyquist plot. Membrane conductivity (κ^m) was calculated by using following equation,

$$\kappa^m = \frac{\Delta x}{AR^m} \quad (5)$$

where Δx is the thickness of membrane, A is the effective surface area of membrane and R^m is the resistance of membrane.

Activation energy (E_a) of membrane was estimated by plotting the graph between $\ln \kappa^m$ (S cm^{-1}) vs 1000 T^{-1} (K^{-1}) using following equation,

$$E_a = -b \times R \quad (6)$$

where b is the slop of the regression line and R is the gas constant ($8.314\text{ J K}^{-1}\text{ mol}^{-1}$).

S6. Methanol Permeability

Methanol permeability of the composite membranes was determined in a diaphragm diffusion cell, consisting of two compartments (80 cm^3) separated by a vertical membrane with 20 cm^2 effective area. The membrane was clamped between both compartments, which were stirred during the experiments. Before the experiment, membranes were equilibrated in water-methanol mixture for 12 h. At the beginning, one compartment (A) was filled with 8M methanol, and the other compartment (B) was filled with double distilled water. Methanol flux arises across the

membrane as a result of concentration difference between two compartments. The increase in methanol concentration with time in compartment B was monitored by measuring the refractive index using a digital refractometer (Mettler Toledo RE40D refractometer). The methanol permeability (P) finally was obtained by the equation given below:

$$P = \frac{1}{A} \frac{C_{B(t)}}{C_A(t-t_0)} V_B l \quad (7)$$

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 , $C_A(t-t_0)$ 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 temperature, and the uncertainty of the measured values was less than 2%.

Table S1. Burst strength, oxidative and hydrolytic stability of NSBC/NMPSGO composite membranes.

Membrane	Burst strength (Kg/cm²)	Oxidative stability (wt% loss)	Hydrolytic stability (wt% loss)
NSBC/NMPSGO-0	1.35	1.98	0.48
NSBC/NMPSGO-4	1.74	2.24	0.94
NSBC/NMPSGO-6	1.89	2.86	1.32
NSBC/NMPSGO-8	2.24	3.14	1.65
NSBC/GO-8	1.71	3.38	1.86

Table S2. Total, bulk and bound water content of different composite membranes and Nafion117 membrane.

Membrane	Total water (%)	Bulk water^a (%)	Bound water^b (%)
NSBC/NMPSGO-0	35.76	34.22	1.54
NSBC/NMPSGO-4	45.93	43.15	2.78
NSBC/NMPSGO-6	58.83	55.69	3.14
NSBC/NMPSGO-8	69.98	65.56	4.42
NSBC/GO -8	32.76	30.43	2.33
Nafion117	41.60	40.56	1.04

^a Bulk water = total water - bound water. ^b Bound water was determined by percent weight loss in TGA between 100 to 150 °C temperature.

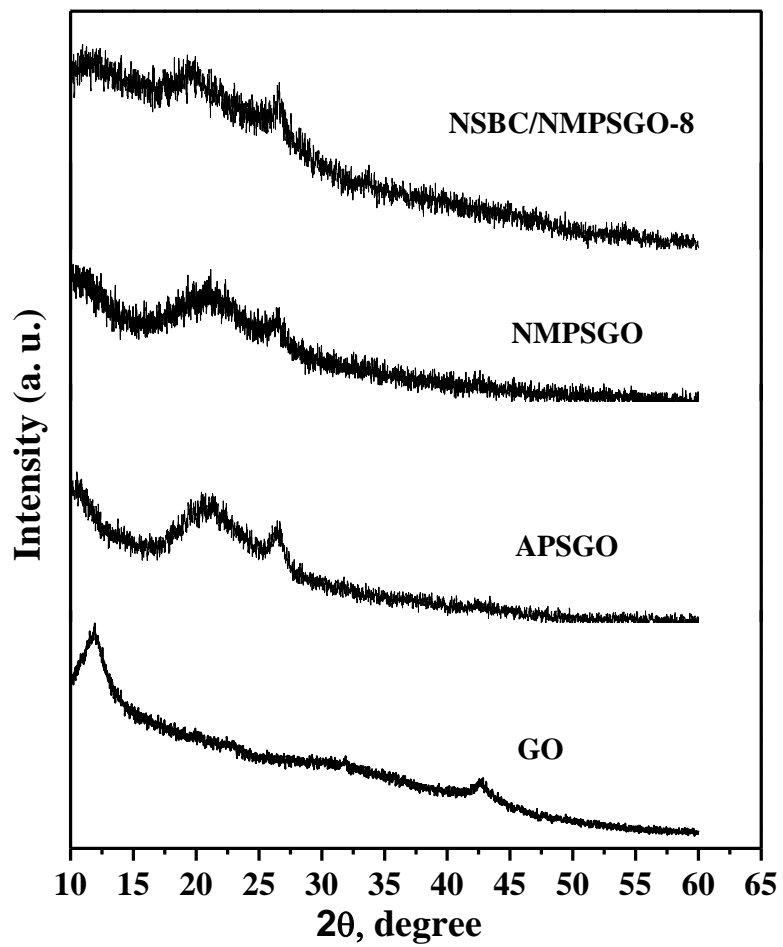


Fig.S1 WXR D patterns of GO, APSGO, NMPSGO and composite membrane (NSBC/NMPSGO-8).

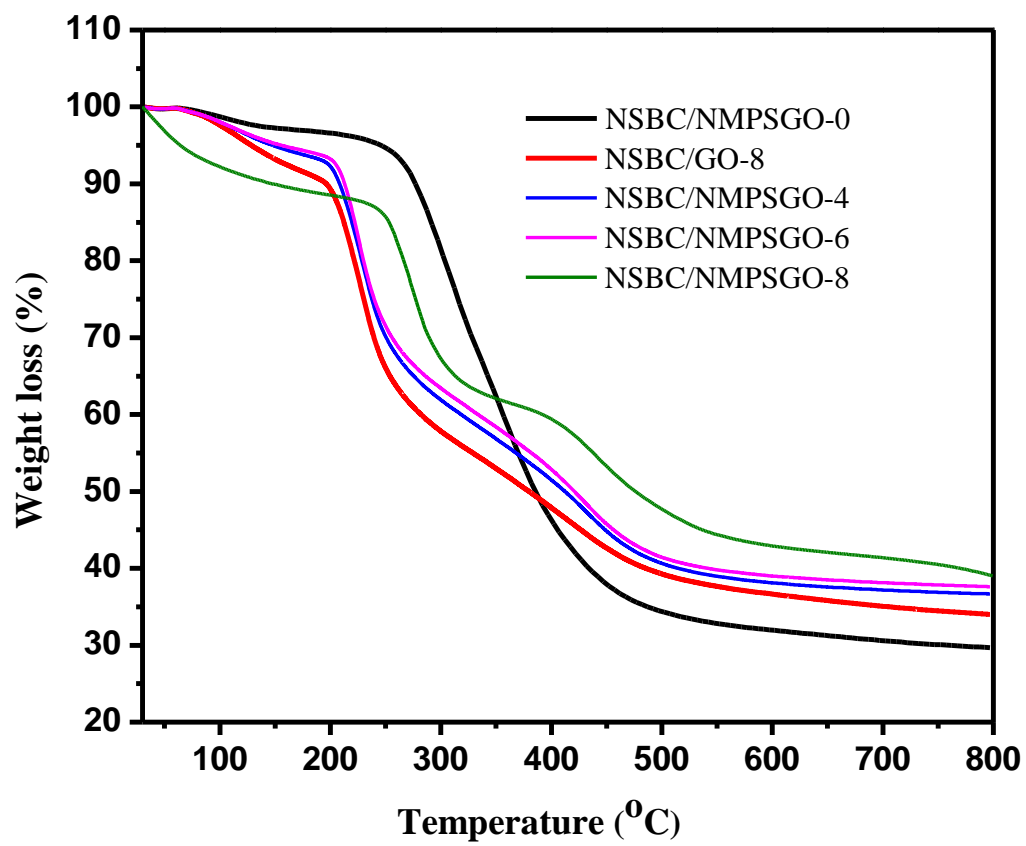


Fig.S2 TGA curves of different composite membranes.

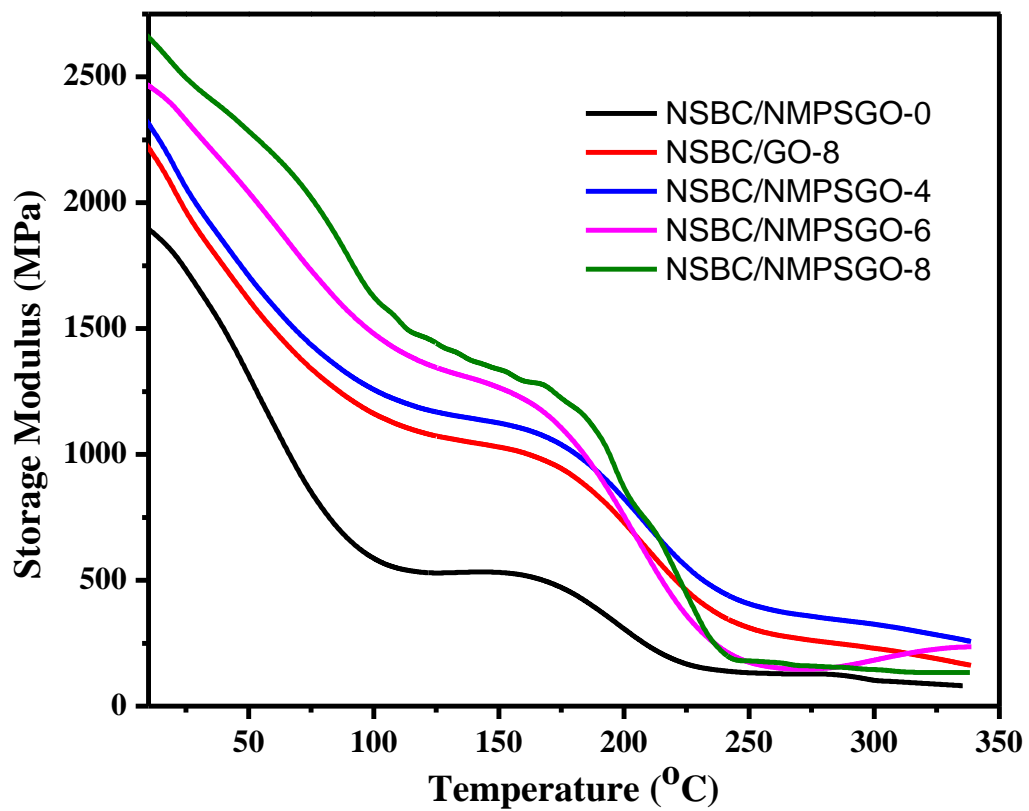


Fig.S3 DMA analysis of NSBC/NMPSGO composite membranes.

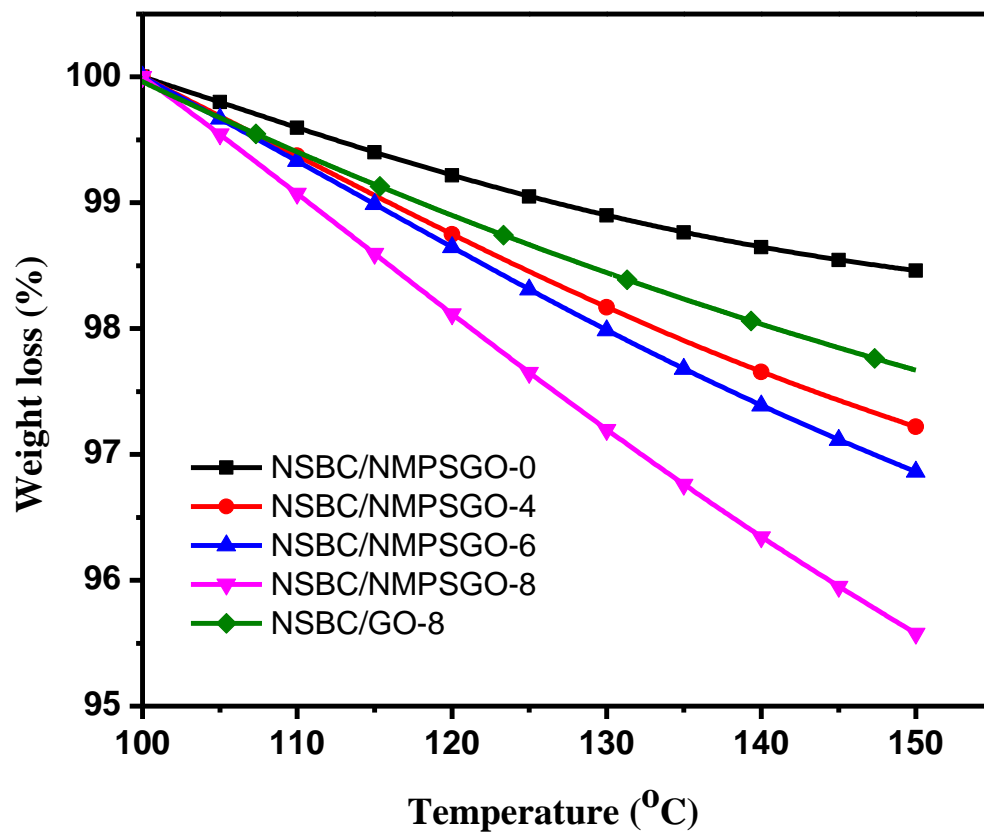


Fig.S4 The bound water content comparison of different composite membranes.