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Supporting Information

Development of robust proton exchange membranes using sPVA-Silica composite with different crosslinkers and evaluation of their fuel cell performance

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Note S1: EXPERIMENTAL PROCEDURES

The oxidative stability, water uptake study, gel fraction study, ion exchange capacity (IEC), dielectric properties, proton conductivity and fuel cell performance are the core studies to evaluate the PEM materials. The resulting sPVA-Si/FA, sPVA-Si/GA, sPVA-Si/PSSA-MA and sPVA-Si/TEOS crosslinked composite membranes are employed for these studies.

Oxidative stability

To assess the oxidative stability of the crosslinked membranes, the uniform size and thickness of the developed membranes were soaked at 80 °C in Fenton's reagent (3% H_2O_2 and $FeSO_4$). By recording the percentage of the remaining weight (RW %) and change in ion exchange capacity (IEC) values, the oxidative stability of the developed membranes was determined.

Water uptake and swelling ratio

The water uptake values of PEMs play an important role on the proton conductivity of the membranes. Thus, the water uptake values of the developed crosslinked membranes were determined using the samples of uniform size and shape by heating at 110 °C for one hour in a hot air oven, and recorded the weights of the dry membranes. The samples were then immersed in deionized distilled water for 24 h at different temperatures. The wet membranes were removed from the water and surface water droplets were carefully wiped off as quickly as possible, and the weights of the wet membranes were recorded. The percent of water uptake of membranes was determined using Equation 1.

$$\text{Water Uptake (\%)} = (W_{wet} - W_{dry}) / W_{dry} \times 100. \quad (1)$$

Where, W_{wet} and W_{dry} are the weights of wet and dry membranes, respectively.

Similarly, the dimensional stability of the developed membranes was assessed by determining the percent of swelling ratio using Equation 2.

$$\text{Swelling Ratio (\%)} = (L_{wet} - L_{dry}) / L_{dry} \times 100. \quad (2)$$

Where, L_{wet} and L_{dry} are the respective average lengths of wet and dry membranes.

Gel fraction study

The gel fraction of the developed membrane was determined using Soxhlet method. Each membrane sample was cut circularly with an area of 2 cm^2. The pieces were dried in a vacuum oven at 60 °C till a constant weight was achieved and were designated as W_{dry}. The dried membranes were then subjected to Soxhlet extraction with deionized water as solvent. After 4 h of extraction, the membranes were dried again in a vacuum oven at 60 °C till a constant weight was obtained and the resulting membrane samples were designated as W'_{dry}. The percent of sol fraction of the resulting membrane was calculated using Equation 3.

$$\text{Sol fraction (\%)} = (W_{dry} - W'_{dry}) / W_{dry} \times 100. \quad (3)$$

Where W_{dry} and W'_{dry} are the weights of dry membrane and extracted dry membrane, respectively.

Based on the percent of sol fraction values, we have further calculated the percent of gel fraction of the resulting crosslinked membrane using Equation 4.

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction}. \quad (4)$$

Ion exchange capacity

Ion exchange capacity is the measure of active ionizable groups present in the membrane, this was estimated by employing the back titration method. Briefly, 1.0 g of membrane samples were dried and immersed in saturated solution of NaCl to replace the protons of sulfonic acid groups with the sodium ions. The replaced protons were then titrated with 0.1 N solution of NaOH using phenolphthalein as an indicator. The number of moles of protons are equal to number of moles of sulfonic groups in the membranes, and thus the IEC values were calculated using Equation 5.

$$IEC_{(meq/g)} = (\Delta V \times C) / W_s. \quad (5)$$

Where, ΔV is the volume of NaOH solution consumed, C is the concentration of NaOH solution and W_s is the dry weight of the sample.

Area resistance

The area resistance of the crosslinked membranes in an aqueous NaCl solution at room temperature was determined using four electrodes - two compartment cell setup. The four electrodes of impedance analyzer were connected to conductivity cell filled with 25 mL of 0.M N NaCl solution as shown in Fig. S1. The developed crosslinked membrane of 1 cm^2 area was placed between the two compartments through membrane holder. The values of resistance after and before placing membrane were recorded and the difference between these two values gives the area resistance of the resulting crosslinked membrane.

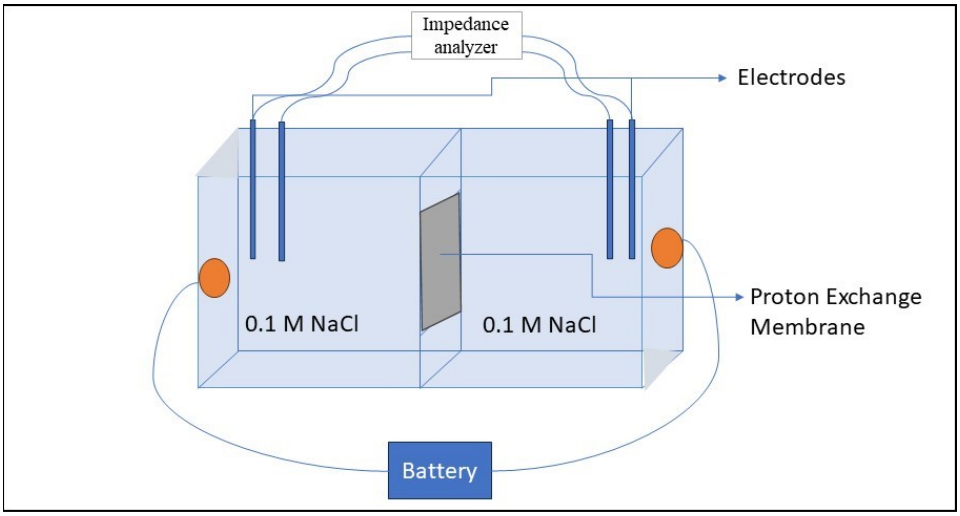

Fig. S1 The schematic diagram of the two compartment cell setup with four electrodes.

Dielectric studies

The dielectric properties of the resulting membranes were studied by employing an AC Impedance Analyzer (Model: Solatron 1260 Impedance/Gain Phase Analyzer, Solatron Analytical, UK) at different temperatures, ranging from 25 to 80 °C with relative humidity of 100% along the in-plane direction over a frequency range of 0.5 Hz to 25 kHz using a conductivity cell.

Proton conductivity

The proton conductivity of the developed hydrophilic crosslinked membranes was measured using an AC Impedance Analyzer (Model: Solatron 1260 Impedance/Gain Phase Analyzer, Solatron Analytical, UK) at the different temperatures, ranging from 25 to 80 °C with relative humidity of 100% along the in-plane direction over a frequency range of 0.5 Hz to 25 kHz using a conductivity cell. Prior to measurement, the

membrane samples were equilibrated at specific temperature and humidity for 1 h in a temperature chamber with humidity controller (ESPEC, SH-241). The proton conductivity of the resulting crosslinked membrane was determined using Equation 6.

$$\sigma\ (S/cm) = L / (R \times A). \quad (6)$$

Where, L is thickness of the membrane (distance between the electrodes), R is the resistance of the membrane, which was calculated using the intercept value of x-axis in the electrochemical impedance spectroscopy (EIS) curve composed of the real value (Z') versus the imaginary value (Z"), and A is the surface area of the membrane.

Fuel cell performance

The fuel cell performance of the developed crosslinked membrane was evaluated employing membrane electrode assembly (MEA) in the fuel cell workstation (Model: FCTS120, Fuel Cell Technologies, Inc. USA). The carbon cloth was used for gas diffusion layer, pasted with 40 wt% of Pt/C (0.4 mg Pt/cm^2) as a catalyst and Nafion as a binder were used for the fabrication of PEM- MEA. The graphite blocks with serpentine flow-pattern were used as current collectors. The electrodes were used as the cathode and the anode by interposing the PEM-MEA. The effective area of the membrane in PEM-MEA was 5 cm^2. The gas humidity chambers were humidified using gases (H_2 and O_2) at 80 °C. The cell performance of the developed crosslinked membranes was evaluated between 0.2 and 1.0 V at 80 °C with pressure of 1 atm by purging oxygen (500 cm^3/min) and hydrogen (250 cm^3/min) gases to cathode and anode, respectively.

Note S2: RESULTS AND DISCUSSION

Particle size analyzer

Particle size analyzer was used to measure the particle size (hydraulic radius) of the nano particles. We have measured the particle sizes of nano-silica and sulfonated nano-silica, the results are presented in Fig. S2. From the results, it is found that hydraulic radius (particle size) of nano-silica was increased after sulfonation from 55 to 140 nm. This is because of replacement of -OH group by -SO_3H group which is more interactive in aqueous media and bulkier than -OH group. Thus, it confirms the successful sulfonation of nano-silica particles. Thus, incorporation of sulfonated nano silica will increase the density of ion exchange groups, intern improves the proton exchange capacity of the membrane.

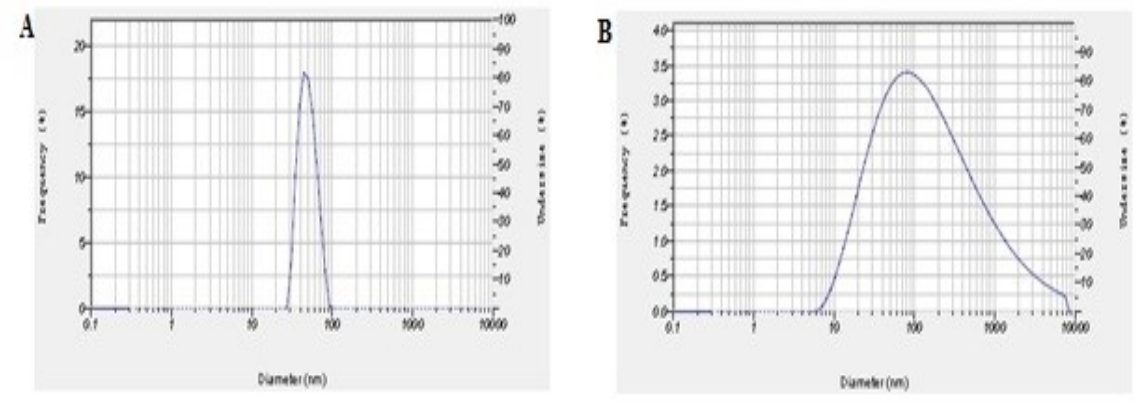

Fig. S2 The particle size analysis of (A) nano-silica particles, (B) sulfonated nano-silica particles.

^{1}H NMR spectroscopy

The sulfonation of PVA was ascertained using ^{1}H NMR spectrometer. The spectrum sPVA was recorded in DMSO-D6 solvent as shown in Fig. S3. A peak resonated at 4.95 ppm was assigned to hydrogen atoms, which are adjacent to the sulphonic groups. The peaks were observed for protons at 7.25 ppm for CH_3 protons and SO_3H protons at 4.95 ppm, the solvent protons at 2.08 ppm. These data confirm the sPVA and presence of sulfonic groups in the developed membrane matrix. The results of ^{1}H NMR are in good agreement with the results of FTIR and particle size analyzer studies.

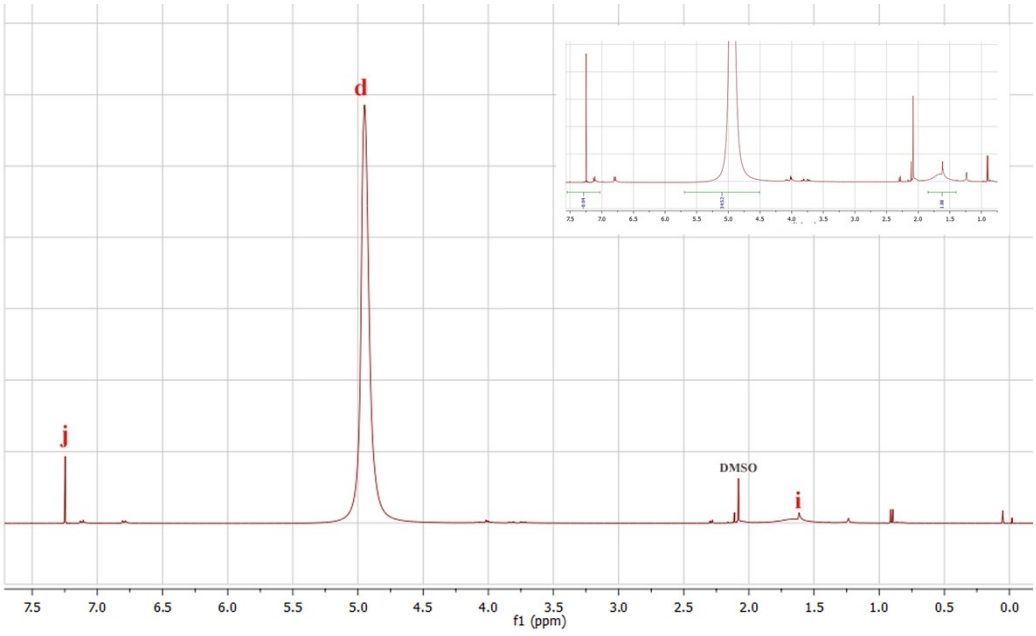

Fig. S3 The ^{1}H NMR spectrum sPVA polymer.

From the spectrum, it is observed that degree of sulfonation (DS) of the sPVA is 56%. The DS was determined from the integral ratios of proton peaks to proton attached on the sulfonated unit (d) and protons attached on the non-sulfonated unit (i and j). The DS was calculated using Equation 7.

$$DS\ (\%) = A_d / (A_{i,j}/ 2). \quad (7)$$

Where, A_d and $A_{i,j}$ are the respective areas of peaks d and I j.

Surface morphology

The surface morphology and the topography of developed hybrid membranes were recorded using atomic force microscope (AFM). The resulting AFM micrographs displayed in Fig. S4(A, B, C and D). From the micrographs it is observed that each crosslinkers act differently with sPVA-Si and forms unique topography in resulting crosslinked membranes. The TEOS crosslinked membrane exhibited tube like structure which may helps to improve transport of proton through the membrane matrix. The images revealed the homogeneous and uniform nature of all the resulting crosslinked membranes.

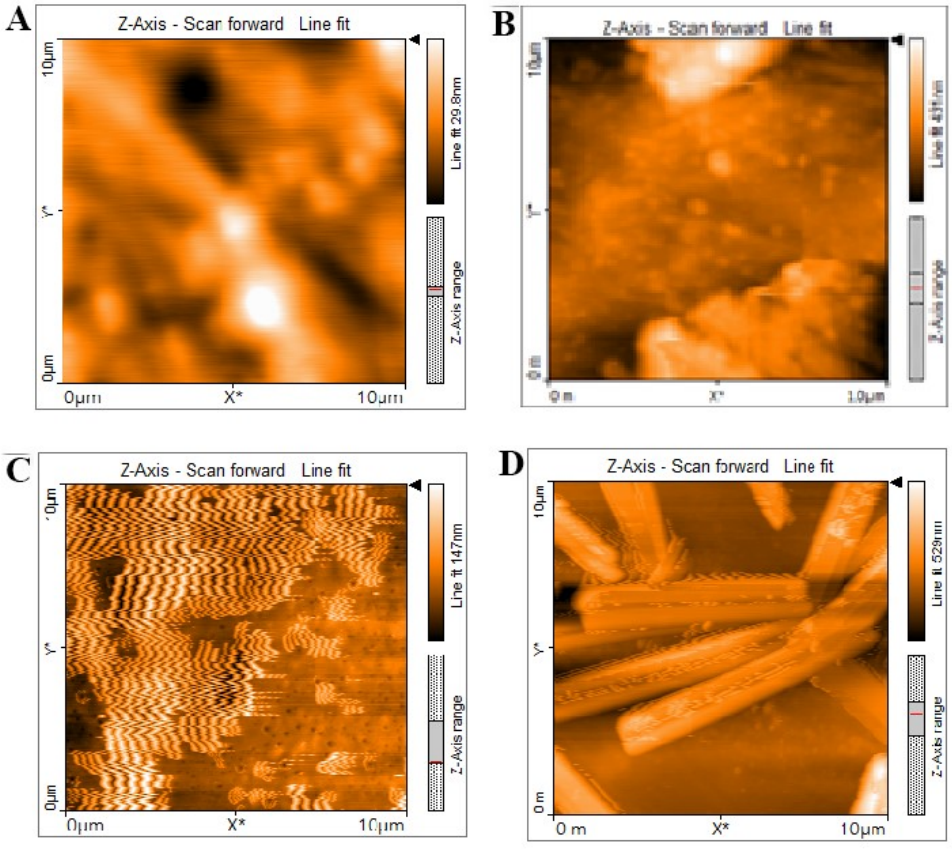

Fig. S4 The AFM images of the sPVA-Si composite membranes with (A) formaldehyde, (B) glutaraldehyde, (C) poly(styrene sulfonic acid-co-malic acid) (PSSA-MA) and (D) tetraethyl orthosilicate (TEOS) crosslinkers.

Water contact angle

To study the surface hydrophilicity of the developed membranes, we have performed the water contact angle study at the ambient temperature, and the results are projected in Figure 5(A and B) and the values are included in Table S3. The WCA values are lowest for the TEOS crosslinked membrane (WCA = 74 °) compare to other three crosslinked membranes. These results infer that the TEOS crosslinked composite membrane is more hydrophilic. Hence, the attraction of water molecule by the surface of TEOS crosslinked membrane is higher which in turn responsible for the enhancement of proton carrier property in the resulting membrane. The WCA results strongly support the values of water uptake and swelling studies.

Thermal stability

To investigate the thermal stability of the developed crosslinked membranes, all the membranes were subjected to thermogravimetric analysis. The TGA and DSC thermograms of sPVA membrane is presented in Fig. S5.

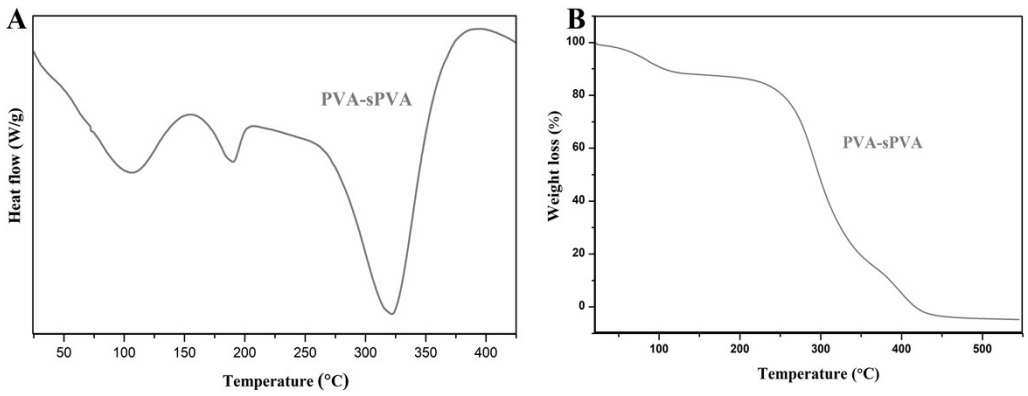

Fig. S5 TGA and DSC thermograms of sPVA membrane.

Area resistance

The area resistance of the crosslinked membranes performed in an aqueous NaCl solution at room temperature gives the primary information on the resistance of the membranes. The results of area resistance of the developed crosslinked membranes in an aqueous 0.1 M NaCl solution at room temperature are included in Table S3. From the results, it is observed that among the developed

crosslinked membranes area resistance of the sPVA-Si/TEOS membrane was significantly lower. These results are in good agreement with the results of both ion exchange capacity and water uptake.

Dielectric study (Nyquist Impedance)

The Nyquist impedance data of sPVA-Si/TEOS and sPVA-Si/PSSA-MA crosslinked membranes were determined by performing the dielectric studies using High Frequency AC Impedance Analyzer at different temperatures, ranging from 25 to 80 °C with relative humidity of 100% along the in-plane direction over a frequency range of 0.5 Hz to 25 kHz using a conductivity cell. To avoid the overcrowding of results of sPVA-Si/TEOS and sPVA-Si/PSSA-MA crosslinked membranes, only at 80 °C are presented in Fig. S6. It is observed that the impedance for sPVA-Si/TEOS crosslinked membrane was significantly low compare to sPVA-Si/PSSA-MA crosslinked membrane. This clearly signifies that the developed sPVA-Si/TEOS membrane demonstrated an excellent conductivity. These results are in good agreement with the results of ion exchange capacity, proton conductivity, area resistance and water uptake.

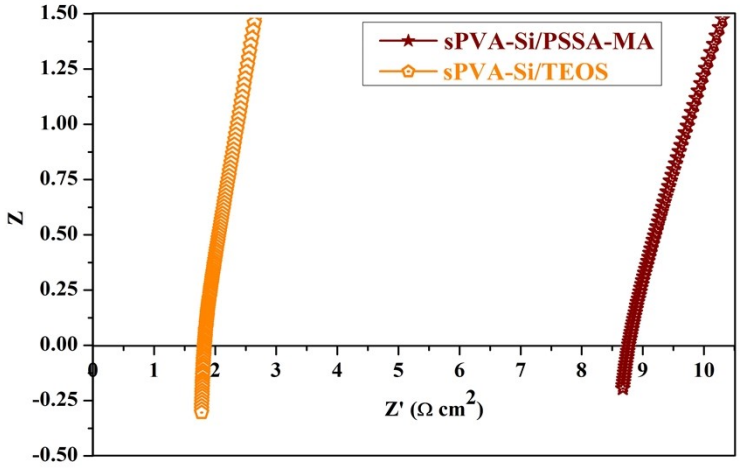

Fig. S6 The Nyquist Impedance plots of sPVA-Si/PSSA-MA and sPVA-Si/TEOS crosslinked membranes at 80 °C.

Mechanical stability, water uptake, swelling ratio, gel fraction, contact angle, area resistance, oxidative stability and ion exchange capacity

The data obtained from mechanical stability, water uptake, swelling ratio, gel fraction, water contact angle analysis, area resistance, oxidative stability and ion exchange capacity of the resulting sPVA-Si/FA, sPVA-Si/GA, sPVA-Si/PSSA-MA and sPVA-Si/TEOS crosslinked composite membranes are presented in Table S1 to S3. The results on these data were discussed in the main manuscript.

Table S1. The mechanical properties of sPVA-Si composite membranes with different crosslinkers.

Membrane	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
sPVA-Si/FA	21.28	73.848	56.752
sPVA-Si/GA	45.84	98.083	228.57
sPVA-Si/PSSA-MA	52.45	86.04	360.52
sPVA-Si/TEOS	64.52	86.07	514.56

Table S2. The water uptakes and swelling ratios of sPVA-Si composite membranes with different crosslinkers.

Membrane	Water Uptake (%)		Swelling Ratio (%)		Gel Fraction (%)	
	25 ℃	80 ℃	25 ℃	80 ℃	Sol	Gel
sPVA-Si/FA	49.65	--	26.56	--	--	--
sPVA-Si/GA	45.56	--	24.05	--	--	--
sPVA-Si/PSSA-MA	42.85	58.33	22.26	31.71	14.56	85.44
sPVA-Si/TEOS	23.91	71.81	16.97	37.95	12.25	87.75

Table S3. The ion exchange capacities and contact angles of sPVA-Si composite membranes with different crosslinkers.

Membrane	Ion Exchange Capacity (meq/g)	Oxidative Stability		Water Contact Angle (degree)	Area Resistance (Ω cm^2)
		RW%	IEC loss (%)		
sPVA-Si/FA	0.48	61.7	--	84	2.68
sPVA-Si/GA	0.64	79	--	81.4	2.26
sPVA-Si/PSSA-MA	0.95	96.6	8.7	76.3	1.59
sPVA-Si/TEOS	1.10	98.2	6.5	74.5	0.56

Note: RW%- Percentage of remaining weight

These results ascertained that the TEOS crosslinked membrane demonstrated the highest thermal, mechanical and chemical stability as compared to other crosslinked membranes including sPVA-Si composite membrane. Consequently, the fuel cell performance of the TEOS crosslinked membrane was greatly enhanced. It is therefore concluded that TEOS is the most suitable crosslinker for silica incorporated sulfonated hydrophilic PVA membrane, and the resulting sPVA-Si/TEOS crosslinked membrane could be employed as potential candidate for the fuel cell application.

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