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Sulfonated PVA / PBI Based Crosslinked Composites Towards Anhydrous Proton Conductive Polymer Electrolyte Membranes for Fuel Cells

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Polymer electrolyte membrane fuel cells (PEMFCs) are being considered as highly promising future energy source due to their high-energy conversion efficiency and their ability to address the environmental concerns related to current energy production. Polymer electrolyte membrane (PEM) is recognized as the key element for an efficient PEMFC. Chemically cross-linked composite membranes consisting of a sulfonated poly(vinyl alcohol) and polybenzimidazole have been prepared by solution casting and were evaluated as proton conducting polymer electrolytes for fuel cell application. All the raw materials used for the preparation of these membranes are environment friendly and these composite membranes are expected to provide the requisite properties for their successful application in fuel cells for energy production specifically owing to their high proton conductivity without much reliance on membrane hydration and low methanol permeability. The best resistance to methanol permeability was observed to be in the order of 10^{-8} cm^2/s and the best proton conductivity was observed to be in the order of 10^{-3} S/cm for the prepared PEMs.

Keywords: Heterocyclic protogenic solvent; Crosslinked polymer electrolyte membrane; Proton conductivity, Sulfonated PVA, polybenzimidazole

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are the most promising candidates as power generators for portable devices due to their high energy density, ease in handling and availability of the necessary storage and supply infrastructure. Nafion® belongs to the perfluorinated class of polymer electrolytes and is by far one of the best performing low temperature polymer electrolyte membrane; they have high conductivity of around 0.08 Scm^{-1} together with good chemical and mechanical stability for fuel cell applications. The Nafion® membranes when used in DMFCs suffer from a drawback of methanol crossover which necessitates the use of a thicker membrane and hence affects their performance adversely [1,2].

An approach to make the polymer electrolyte membrane technically and economically competitive is to use an electrolyte system in which the reliance of the proton conductivity on the presence of water can be minimized in order to be able use these electrolyte membranes at high temperatures. The use of nitrogen containing heterocyclic molecules as proton solvents in polymer electrolyte membranes is a promising approach since due to the amphoteric nature of these molecules they can form intermolecular hydrogen bonds and undergo self-dissociation [3,4]. The utilization of polymers of heterocyclic molecules along with other eco-friendly polymer/biopolymers with acidic groups which can provide protonic conductivity is an extremely interesting proposition which we have tried to explore in the present work. Studies on proton conducting polymer electrolyte networks consisting of alginic acid (AA) and heterocyclic molecules such as imidazole and 1H-1,2,4-triazole [5,6] suggest that these materials are potential candidates for fuel cell membranes.

Poly benzimidazole (PBI) has attractive properties for high temperature fuel cell application owing to its excellent thermal and mechanical property, low gas permeability and good CO tolerance. For quite some time acid doped poly [m-phenylene-bis(5,5’-benzimidazole)] has evolved as a promising polymer electrolyte membrane material for high temperature fuel cells. PBI is a basic polymer and has good chemical and thermal stability owing to its rigid aromatic backbone. In PBI/acid systems the proton conductivity depends strongly on the level of acid doping [7,8] that is the number of acidic molecules per repeating unit of the polymer. Several strategies have been adopted to improve upon the properties of PBI/phosphoric acid membrane systems which include the synthesis of structural analogues of PBI [9], preparation of composite PBI membranes [10] and chemically cross-linked membranes [11], etc. PBI shows good proton conductivity when doped with phosphoric acid (PA) but losses its mechanical properties significantly which makes the MEA fabrication quite challenging. Incorporation of sulfonated PVA instead of PA to impart proton conductivity to the PBI membrane without significant degradation in its mechanical property is an attractive option.

Poly(vinyl alcohol) (PVA) has an excellent resistance to methanol crossover and here it appears to be a potential material to be utilized in the preparation of a polymer electrolyte membrane with low methanol permeability [12]. PVA membranes have demonstrated to have the mechanical and chemical stability which are adequate for their utilization in the preparation of polymer electrolyte membranes [13]. PVA itself does not have an ionic group however several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be incorporated to impart hydrophilicity and/or ionic groups [14,15]. Several crosslinking methods for PVA have been published for different use, since in general all multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain three-dimensional networks in PVA [16].

Our work here studies the properties of chemically cross-linked membranes prepared from PBI and acidic polymers like sulfonated poly(vinyl alcohol). Such composite membranes are expected to exhibit improved mechanical strength and chemical stability, allowing for higher acidic groups levels and therefore high conductivity and better fuel cell performance.

2. EXPERIMENTAL

2.1. Materials

Poly (vinyl alcohol), Average Mol. Wt. - 1,25,000 and degree of hydrolysis 99 % was obtained from Sigma Aldrich. Polybenzimidazole (PBI) (Grade - 0.8 IV polymer) was obtained from PBI Performance Products Inc., USA. Glutaraldehyde (25 % aqueous solution) and Chlorosulfonic Acid (97 % for synthesis) was obtained from LobaChemi, India, Dichloroethane and Methanol was obtained from Scharlau, Spain. All chemicals were used as received without any further purification. Millipore water was used throughout the study.

2.2. Preparation of the composite polymer electrolyte membranes

The polymer solutions were prepared by dissolving PVA and PBI in DMSO at 80 ^{o}C with continuous stirring. The polymer solution were allowed to cool to ambient temperatures before being mixed in appropriate proportions and were stirred at room temperature (25 ^{o}C) to obtain a homogeneous blend solution. The requisite amount of the chlorosulfonic acid reagent (CSR) was added drop wise and the solution stirred further. To this homogeneous polymer solution desired amount of the glutaraldehyde (GA) crosslinking reagent was added and the solution was further stirred for few minutes. After this, the homogeneous solution was poured onto glass petridish and allowed to dry at 45 - 50 ^{o}C for several days. The dried membranes were peeled off the glass substrate and the obtained membranes were approximately 100 - 150 μm in thickness.

2.3. Characterization techniques

2.3.1. FTIR Spectroscopy

FTIR spectra of the pure polymer membranes and the composite membranes was obtained with Nicolet iS10 FTIR Spectrometer in the range of 4000 - 600 cm^{-1} using Omnic Software, a uniform resolution of 2 cm^{-1} was maintained during the collection of the spectral data.

2.3.2. Water Uptake Measurements

Water uptake of the cross-linked polymer electrolyte membranes was determined by measuring the change in the weight before and after hydration. The membranes were equilibrated in deionized water for 24 hours at 25 ^{o}C, and the surface attached water on the membrane was removed carefully by placing both the surfaces of the membranes gently over a filter paper. The weight of the wetted membrane was determined using an analytical balance with a sensitivity of 0.1 mg. Water uptake was calculated by using the following equation:

$$Water \quad uptake = \frac{M_w - M_d}{M_d} \tag{1}$$

where M_w and M_d is the weight of the hydrated polymer and dry polymer in grams respectively.

2.3.3. Methanol Permeability Measurement

The measurement of Methanol Diffusion Co-efficient through the composite membranes was performed using a diffusion cell having two compartments which was separated by the membrane situated horizontally. Prior to Diffusion Co-efficient measurement, the membranes were equilibrated in aqueous methanol solution 50 % v/v for 24 hours and the experiments were carried out at room temperature (25 ^{o}C). The methanol concentration of the receptor compartment was estimated using a differential refractometer (Photal OTSUKA Electronics, DRM-1021); the differential refractometer is highly sensitive to the presence of methanol. The change in refractive index of the diffusion samples were averaged over 52 scans in the differential refractometer to determine the change in refractive index. The methanol Diffusion Co-efficients for the PEMs was calculated using the following equation [17]:

$$D = \frac{lV_{\text{sample}}}{\mathrm{A}t_{\exp}} \ln \frac{C_1 - C_{\text{methanol}}}{\mathrm{C}_2 - \mathrm{C}_{\text{methanol}}} \tag{2}$$

where D is the methanol diffusion coefficient, l is the thickness of the membrane, V_{sample} is the volume of the sample solution; A is the cross-section area of membrane and t_{exp} is the time interval during which diffusion occurs, C_{methanol} is concentration of methanol fed in the donor compartment, C_1 is concentration of methanol in receptor compartment at t = 0 and C_2 is the concentration of methanol in the receptor compartment at $t = t_{exp.}$

2.4. Mechanical properties

The tensile strength of the composite membranes was carried out using Hounsfield H10KS tensile testing machine at a crosshead speed of 12.5 mm/min, temperature 27 ^{o}C and 75 % humidity. The gauge dimension of the test samples was 5 mm x 50 mm. For each sample, three specimens were tested to determine the average value of tensile strength and percent elongation at break.

2.5. Thermo-gravimetric Analysis

To determine the thermal stability of the composite membranes, thermogravimetric analysis of the pristine polymers and the composite membranes was carried out by using Mettler Toledo TGA/DSC Star System, at a heating rate of 10 ^{o}C /min, with nitrogen flushed at 80 ml/min.

2.6. Impedance Spectroscopy

The membrane was sandwiched between stainless steel electrodes; AC impedance spectra of the membranes at a particular temperature was obtained by using Agilent 4294A Precision Impedance Analyzer under an oscillation potential of 10 mV from 40 Hz to 10 MHz [18]. The conductivity was calculated from the bulk resistance obtained from the high frequency intercept of the imaginary component of impedance with the real axis. The conductivity of the membrane is calculated using the following equation:

$$\sigma = \frac{l}{RA} \qquad (3)$$

where σ, R , l and A represent membrane conductivity, bulk resistance, membrane thickness and area of the electrode, respectively.

2.7. Scanning Electron Microscopy JSM 6360A

The surface morphology of the PEMs was studied using a JEOL JSM 6360A Scanning Electron Microscope. The surfaces were gold coated to avoid charging and were examined at 20 kV accelerating voltage.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy

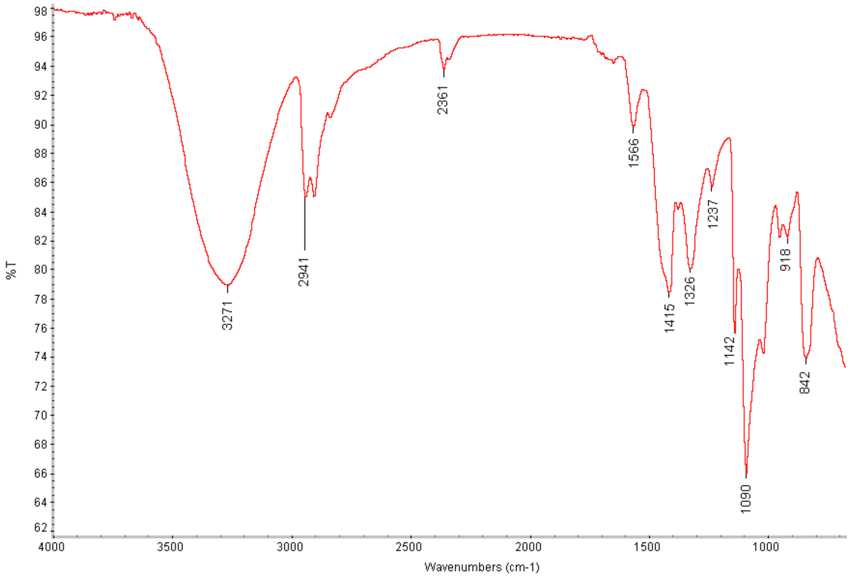

Figure 1. FTIR spectrum of the membranes designated as PEM-1

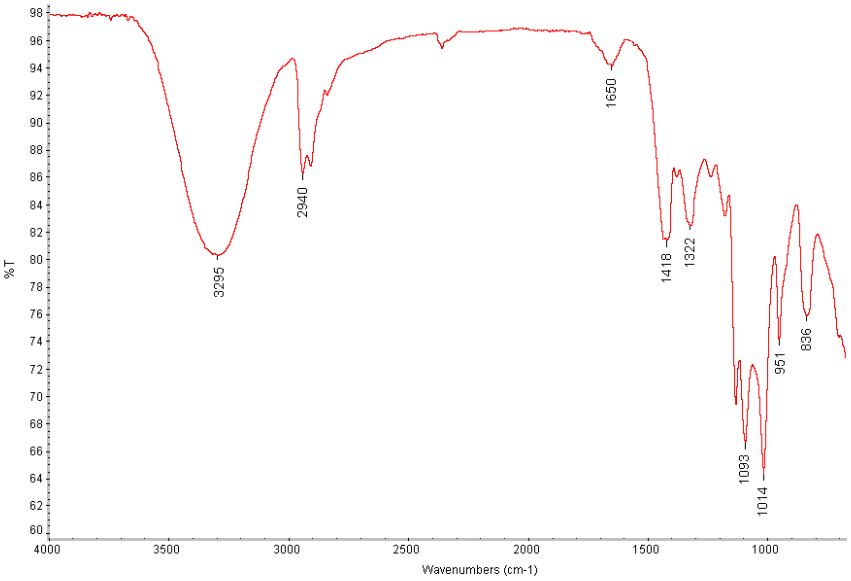

Figure 2. FTIR spectrum of the membranes designated PEM-5

The FTIR spectrum of the Cross linked Pure PVA membrane is showed in Fig. 1 and it clearly depicts the major peaks associated with poly (vinyl alcohol). The C–H broad alkyl stretching band (ν = 2850-3000 cm^{-1}) and typical broad hydroxyl bands for hydrogen bonded alcohol (ν = 3200-3570 cm^{-1}) can be observed in the spectra. Intra-molecular and inter-molecular hydrogen bonding occurs among the PVA chains due to the high hydrophilic forces. The broad absorption band (from ν = 1000 - 1330 cm^{-1}) is attributed to the (C-O) stretching and (C-O-C) asymmetric stretching of alcohol and esters in PVA. An important absorption peak of PVA was verified at ν = 1090 cm^{-1}.

The FTIR spectrum in Fig. 2 shows the spectra associated with the sulfonated PVA membrane cross-linked by glutaraldehyde (SPVA/GA). By crosslinking PVA or SPVA with GA the intensity of the O-H stretching vibration peak (ν = 3200-3400 cm^{-1}) decreased and a shift in peak frequency was also observed. The result suggests the occurrence of the crosslinking reaction at the hydroxyl group sites and that the hydrogen bonding becomes weaker in cross-linked PVA than in pure PVA because of the diminution in the number of OH groups and acetal formation [19]. The absence of the free aldehyde peak (ν = 1640 cm^{-1}) indicates that the aldehyde groups of GA have completely reacted with O-H groups of the PVA. This confirms that GA has acted as a chemical cross-linker among the PVA polymer chains. Presence S=O stretching around 1010 - 1020 cm^{-1} confirms the presence of sulfonic acid group and hence the successful grafting of the sulfonic group at the hydroxyl group sites.

3.2. Water Uptake Measurements

For water uptake measurement of the PEM they should be hydrolytically stability is aqueous environment. The PVA constituent of the prepared PEMs are not stable hydrolytically unless they are cross-linked hence the stability of these PEMs in the aqueous environment further confirms the accomplishment of the chemical crosslinking at the hydroxyl group sites with glutaraldehyde. The results of the water uptake of the prepared PEM are reported in Table - 1. The results show that the water uptake of these cross-linked composite membranes increase with increase in the degree of sulfonation of the polymer matrix which is due to higher affinity of the sulfonic acid groups towards hydration. However with increase in the PBI content of the membranes the water uptake decreases with a particular level of sulfonation and it follows similar trend even at different levels of sulfonation of the polymer matrix. Boroglu et al. reported similar results for 4,4-diaminodiphenyl ether-2,2-disulfonic acid modified PVA membranes where the immobilization of the acids resulted in decrease in the free volume capable of holding the water molecules and hence resulted in decrease in water uptake of the modified membranes with increase in acid content [20]. The highest water uptake of 1.79 g/g was observed for the membrane designated PEM-5 whereas the lowest water uptake of 0.44 g/g was observed for the membrane designated PEM-4.

Table 1. Composition and properties of the PEMs

Membrane ID	PVA Content (g)	PBI Content (g)	CSR Content (ml)	GA Content (ml)	Water Uptake (g/g)	Methanol Permeability (cm^2/s)	Tensile Strength (MPa)	Percent Elongation (%)
PEM-1	2	0	0	0	-	-	47.35	80.2
PEM-2	2	0	3.0	0.5	0.82	2.05×10^{-7}	58.15	51.6
PEM-3	2	0.25	3.0	0.5	0.98	3.84×10^{-7}	38.33	52.4
PEM-4	2	0.50	3.0	0.5	0.44	5.86×10^{-8}	31.08	38.4
PEM-5	2	0	4.5	0.5	1.79	9.15×10^{-6}	24.71	50.1
PEM-6	2	0.25	4.5	0.5	1.36	5.40×10^{-6}	26.68	60.7
PEM-7	2	0.50	4.5	0.5	0.92	1.12×10^{-6}	39.72	82.6

3.3. Methanol Permeability Measurement

The methanol permeability of the prepared PEM was found to be in the range of 10^{-6} to 10^{-8} cm^2/s as reported in Table - 1. The methanol permeability results show that the membranes with higher water uptake that is with a lower degree of effective crosslinking show higher methanol permeability whereas the membranes with low water uptake and hence with a dense and compact morphological structure show comparatively lower values for methanol permeability. The methanol permeability value of 6.5×10^{-6} cm^2/s has been reported for Nafion 117 under similar measurement conditions [21]. Hence these composite membranes generally show better resistance to methanol permeability compared to Nafion under similar experimental conditions.

3.4. Mechanical Properties

The results of the tensile tests are reported in Table -1. The tensile strength of pristine uncross-linked PVA is 47.35 MPa, the tensile strength increases to 58.15 MPa with the incorporation of the chemical crosslinking which restricts the flexibility of the polymer chains and hence decreases the percent elongation and increases the tensile strength of the cross-linked PEM membranes. The incorporation of sulfonated polymer instead of phosphoric acid in PBI composites to some extent helps resolve the usual mechanical stability problems of the PA/PBI composites [22]. At a low level of sulfonation and crosslinking of the polymer matrix the tensile strength of the PEM membranes decreases with increase in PBI content of the membranes which can be attributed to the disruption of the hydrogen bonding's among the PVA polymer chains. When the level of sulfonation of the PVA polymer matrix is increased the tensile strength and percent elongation of the composite PEM increases with increase in PBI content of the membranes. This is due to the fact that at higher level of sulfonation the availability of the crosslinking sites is reduced which results in a less intense crosslinking hence more flexibility in the polymer chains which leads to increase in percent elongation of the polymer chains and also slight improvement in the tensile strength of the cross-linked PEMs.

3.5. Thermo-Gravimetric Analysis

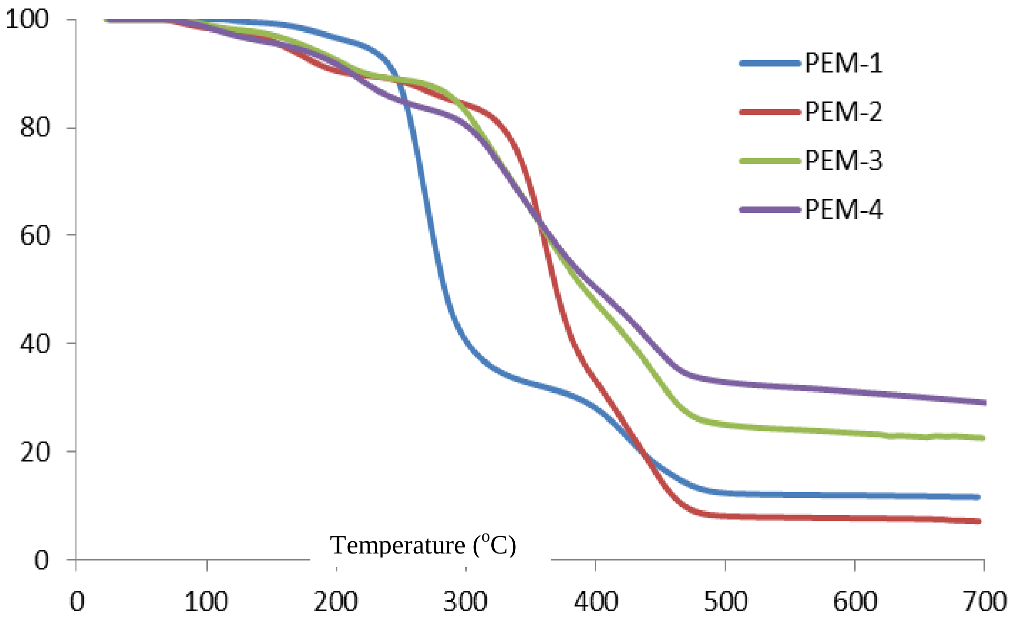

Figure 3. TGA Thermograms of the membranes designated PEM-1, PEM-2, PEM-3 and PEM-4

The thermal stability of the PVA/PBI composite membranes was investigated by thermo gravimetric analysis. The TGA thermograms of the PVA and the PVA/PBI with different degree of sulfonation are showed in Fig. 3 and Fig. 4 respectively. The pristine PVA is thermally stable up to around 250 ^{o}C. The cross-linked PVA/PBI composite membranes show enhancement their thermal stability; the thermal degradation of these composites generally showed two major weight loss steps. The first weight loss is centered around 200 ^{o}C which corresponds to the weight loss of any absorbed water, any water molecules associated with the sulfonic acid groups and water as by-product by further esterification reaction in the composite membranes. The second weight loss is centered around 350 ^{o}C is due to the thermal degradation of the ether and ester crosslinking linkages [20].

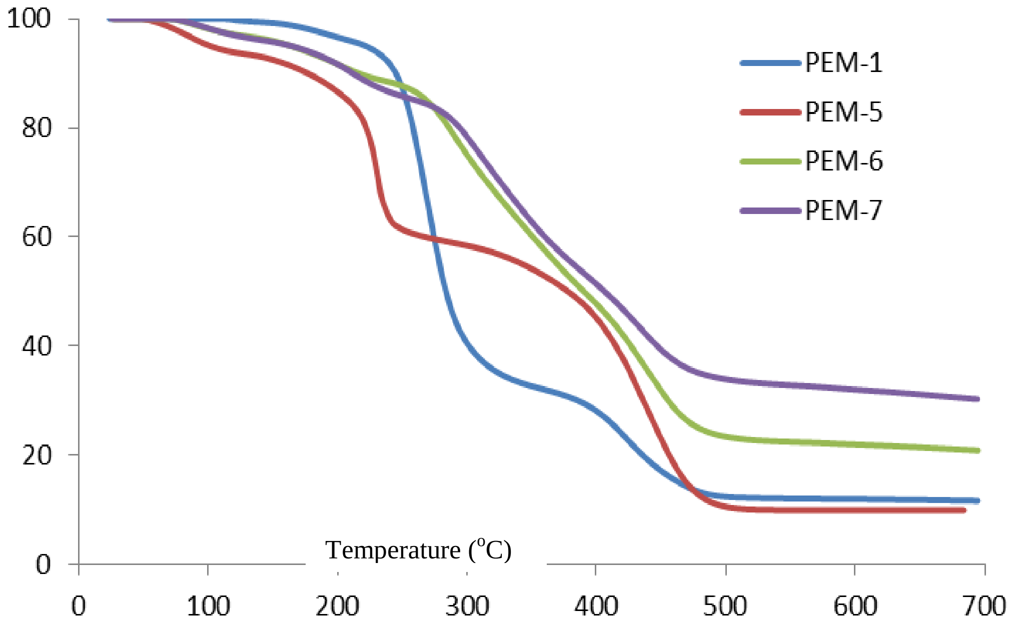

Figure 4. TGA Thermograms of the membranes designated PEM-1, PEM-5, PEM-6 and PEM-7

3.6. Impedance Spectroscopy

The proton conductivity values for the prepared PEMs with different degree of sulfonation and different wt. % PBI content at different temperatures are reported in Table - 2. The best proton conductivity of the prepared cross-linked composite membranes is in the order of 10^{-3} S/cm. The proton conductivity for the pure sulfonated PVA membranes decreases with increase in temperature which is due to gradual loss and absence of the water which helps in the conduction of the protons. However the an increase in conductivity in observed with increase in temperature and well as with the increase in the content of the PBI for the cross-linked PVA/PBI composite membranes since here the presence on the imidazole group provides a conduction path for the protons and hence augments the conductivity of the composite membranes. The best proton conductivity of 2.72 x 10^{-3} S/cm is observed for the composite membrane with the highest degree of sulfonation and PBI content.

Generally proton conduction through polymer electrolytes occurs through two different mechanisms [23,24]. The first mechanism is Grotthuss mechanism where the proton passes through a chain of water molecules transferring from one vehicle to the other via proton hopping. The second mechanism is vehicular mechanism where the proton combines with solvent molecules to produce a complex which then diffuses through the membrane. The nature of hydrogen bonding between the protonated species and their environment dictates the conduction mechanism whereby strong hydrogen bonding system tend to follow Grotthuss mechanism and weaker hydrogen bonding systems show vehicular mechanism.

Table 2. Composition and Proton Conductivity values of the PEMs

Membrane ID	PVA Content (g)	PBI Content (g)	CSR Content (ml)	GA Content (ml)	σ @ 30 °C (S/cm)	σ @ 60 °C (S/cm)	σ @ 90 °C (S/cm)
PEM-1	2	0	0	0	-	-	-
PEM-2	2	0	3.0	0.5	5.47 x 10^{-5}	2.06 x 10^{-5}	6.71 x 10^{-6}
PEM-3	2	0.25	3.0	0.5	4.21 x 10^{-4}	5.26 x 10^{-4}	7.01 x 10^{-4}
PEM-4	2	0.50	3.0	0.5	6.51 x 10^{-4}	7.42 x 10^{-4}	9.50 x 10^{-4}
PEM-5	2	0	4.5	0.5	7.85 x 10^{-5}	7.03 x 10^{-5}	5.85 x 10^{-5}
PEM-6	2	0.25	4.5	0.5	5.89 x 10^{-4}	7.46 x 10^{-4}	1.06 x 10^{-3}
PEM-7	2	0.50	4.5	0.5	5.87 x 10^{-4}	8.09 x 10^{-4}	2.72 x 10^{-3}

3.7. Scanning Electron Microscopy

The surface morphology of the prepared membranes was studied using scanning electron microscopy. Figure 5 shows the scanning electron images of the pristine PVA membrane which shows a smooth and homogeneous membrane surface. The images of the cross-linked composite PVA-PBI membranes are shown in Figure 6 and 7; these images also show a smooth and homogeneous surface. The homogeneity of the surface of these membranes confirms that the polymer matrices are dispersed well and there is no incompatibility among the materials used [22].

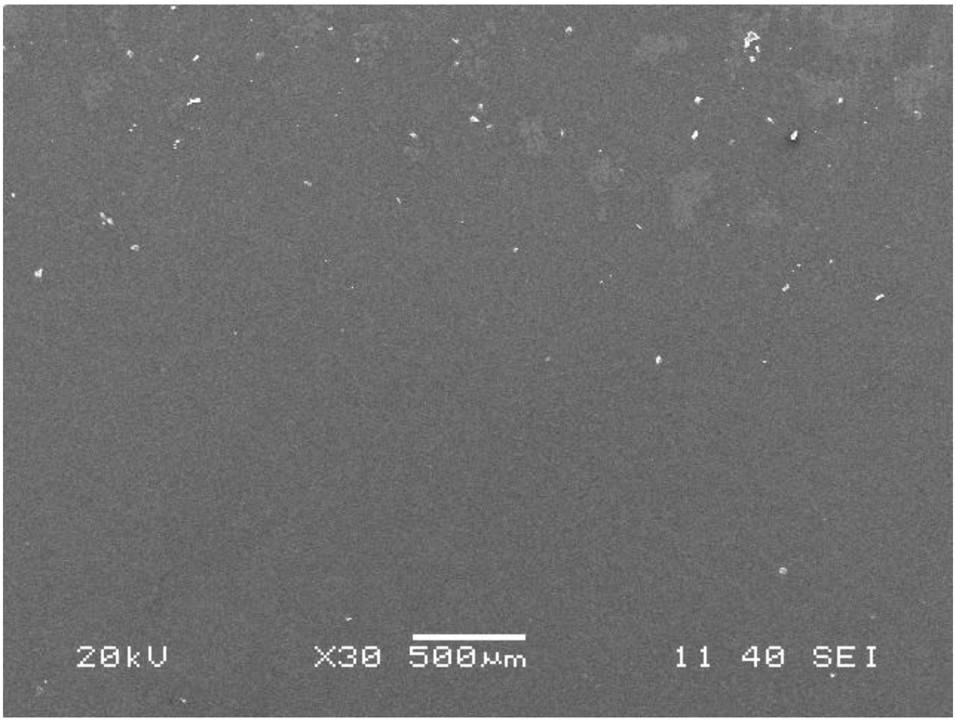

Figure 5. Scanning Electron Image of PEM-1

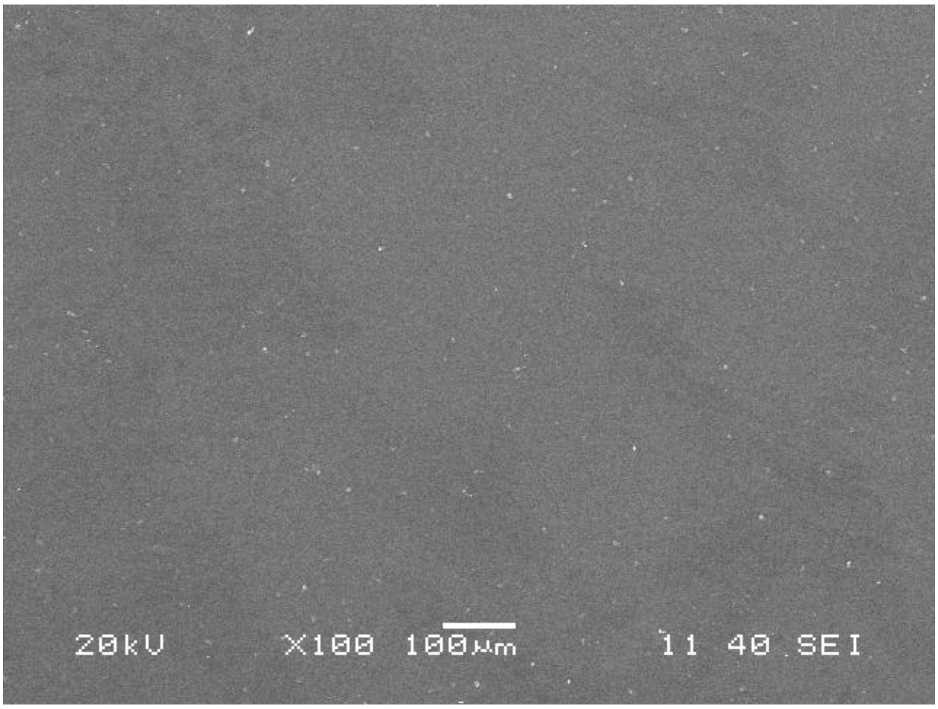

Figure 6. Scanning Electron Image of PEM-6

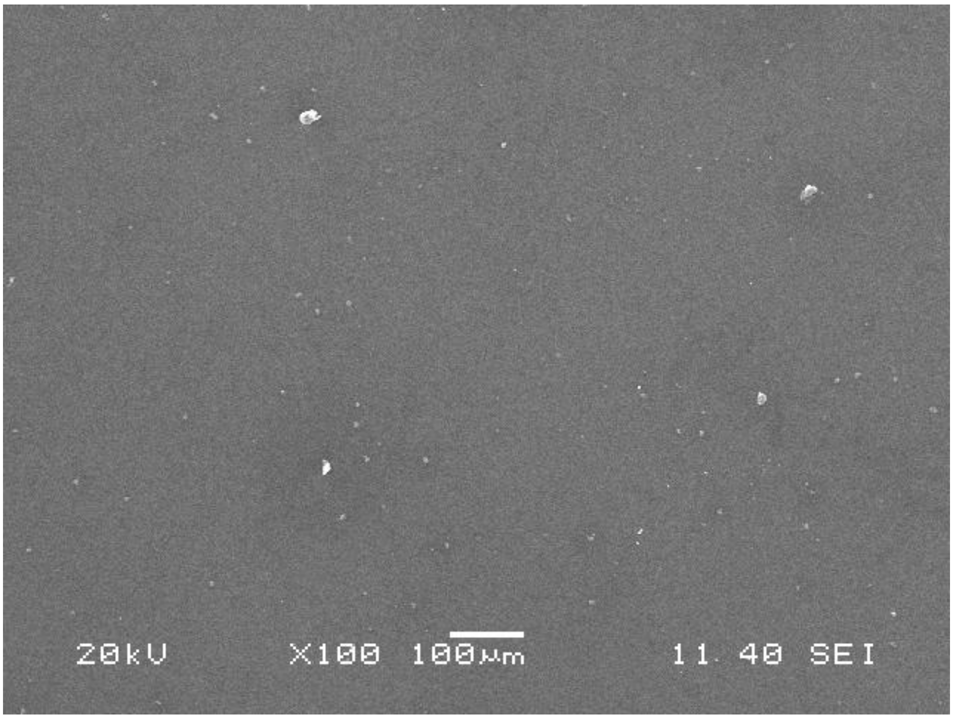

Figure 7. Scanning Electron Image of PEM-7

4. CONCLUSION

PVA/PBI based cross-linked composite membranes were successfully fabricated and studied using various characterization techniques. The FTIR studies confirm the formation of cross-linked networks by the reaction between the hydroxyl groups of PVA and the aldehyde groups of glutaraldehyde. The FTIR studies also confirmed the grafting of the sulfonic acid groups at the hydroxyl group sites of the PVA matrix. The water uptake of the cross-linked composite membranes was studies and the membranes were found to be hydrolytically stable. The best resistance to methanol permeability was observed for the membrane designated as PEM-4 whereas the best proton conductivity was observed for the membrane designated as PEM-7. It was found that increase in degree of sulfonation augments the proton conductivity of the membranes but at the same time has an adverse effect on the capability of the membrane to resist the methanol permeability. All the membranes show smooth surface morphology as observed by SEM.

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