Effect of varying poly(styrene sulfonic acid) content in poly(vinyl alcohol)–poly(styrene sulfonic acid) blend membrane and its ramification in hydrogen–oxygen polymer electrolyte fuel cells

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ABSTRACT

Poly(styrene sulfonic acid) (PSSA) content in poly(vinyl alcohol) (PVA) and PSSA blend membrane is varied and its effect on proton conductivity is studied at varying relative humidity (RH) values. The maximum proton conductivity is observed for the PVA–PSSA membrane with about 35 wt. % PSSA at all humidity values. At 30% RH value, the conductivity of PVA–PSSA blend membrane is 1.20×10^{-3} S/cm, which is about two orders of magnitude higher than the conductivity value of 2.27×10^{-5} S/cm observed for pristine PVA membrane. Water self-diffusion coefficients and water release kinetics of these materials have been characterized by nuclear magnetic resonance (NMR) imaging technique, which validate the use of this membrane in polymer electrolyte fuel cells (PEFCs). A peak power density of 210 mW/cm^2 at a load current-density of 500 mA/cm^2 is achieved for the PEFC with the optimized PVA–PSSA membrane as electrolyte compared to a peak power density of only 38 mW/cm^2 observed at a load current-density of 80 mA/cm^2 for the PEFC with pristine PVA membrane as electrolyte while operating at 75 °C with H$_2$ and O$_2$ feeds to the fuel cell maintained at atmospheric pressure.

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1. Introduction

Among the various fuel cell systems currently under development polymer electrolyte fuel cells (PEFCs) are most advanced and up-coming owing to their amenability to quick start and ambient temperature operation [1]. The membrane electrolyte is a vital component of PEFC and needs to have high specific conductivity, good mechanical, chemical and thermal stability in addition to low cost. At present, membranes made of Nafion®, a perfluorosulfonated polymer with a hydrophobic fluorocarbon backbone and hydrophilic sulfonic acid pendant side chains, happen to be the only commercially available and successfully used membranes in PEFCs. Proton conduction in Nafion® membranes occurs through the ionic channels formed by micro or nano-phase separation between the hydrophilic proton exchange sites and the hydrophobic domains [2]. But Nafion® is expensive and hence has been a limiting factor in commercialization of PEFCs. Accordingly, development of cost-effective proton-conducting membranes with high conductivity of ca. 0.1 S/cm at 50% RH in the temperature range between 60 and 120 °C forms an important area of materials development for PEFCs.

Since its accidental discovery by Haehnel and Herrmann in 1924, poly(vinyl alcohol) (PVA) has become one of the most studied polymers in the literature [3–8]. PVA can be industrially produced rather cheaply; it is non-toxic and can easily form thin, large surface-area membranes, a characteristic most desired of fuel cells. Under acidic conditions, —OH groups of PVA develop chemical cross-linking with aldehydes to form acetal or hemiacetal linkages [9]. PVA membrane itself does not have any negatively charged ions, rendering it a poor proton conductor in relation to commercial available Nafion® membranes. Interestingly, several organic groups like hydroxyl, amine, carboxylate, sulfonate, phenolic, and quaternary ammonium salt can be incorporated with PVA membrane to increase its proton conductivity and hydrophilicity [10–12].

In the literature [13,14], PVA membranes doped with H$_3$PO$_3$ or H$_3$PO$_4$ and phosphotungstic acid (PWA) have been studied. However, as the phosphoric acid is not covalently bound to the polymer matrix, it can leach out of the membrane, resulting in its decreased proton conductivity. PVA–PWA composite membranes, being prone to excessive water swelling, suffer from reduced

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mechanical strength. Xu et al. [15] have incorporated silica particles into PVA–PWA composite membrane to improve the membrane endurance and thermal stability. Rhim et al. [16] have reported PVA cross-linked with sulfosuccinic acid (SSA), a proton conducting material; on optimizing both the cross-linking amount and the cross-linking temperature, the maximum proton conductivity for the membrane is found between 10^{-3} and 10^{-2} S/cm. As an extension to this study, Kim et al. [17] reported a PVA–SSA-silica blend membrane caste through a sol–gel route and reported good proton conductivity even at elevated temperatures. Wu et al. [18] prepared alkaline PVA–poly(acrylic acid) (PVA–PAA) composite membrane with varying PAA content and reported the PVA–PAA composite membrane with the respective composition ratio of 10:5 to exhibit a good balance in its proton conductivity and mechanical strength. Recently, Kang et al. [19] and Kim et al. [20] reported PVA–poly(styrene sulfonic acid-*co*-maleic acid) (PVA–PSSA-MA) composite polymer electrolyte membrane that has controlled membrane charge density and prevents excessive swelling with proton conductivity values of ca. of 10^{-2} S/cm.

In this study, we report PVA–PSSA blend electrolyte membranes developed by a novel sol–gel route with varying PSSA content. To examine the cross-linkage between the PVA and PSSA moieties and the associated water dynamics, we have characterized the PVA–PSSA membranes by various nuclear magnetic resonance (NMR) techniques including imaging [21], water release kinetics and diffusometry. The study reveals higher water retention capability of PVA–PSSA membrane desirable for the membrane electrolyte in polymer electrolyte fuel cells. Water self-diffusion coefficients, as determined by NMR techniques, are contrasted with water release kinetics NMR measurements; the former help investigating localized environments over a typical distance scale of several microns and are sensitive to chemical composition and morphology, while the latter provide insight into the averaged long-range water transport properties over a typical distance scale of hundreds of microns. This contrast provides a bridge between the fundamental understanding of the composition and morphological structure of the membrane on the one hand and the impact of these factors on transport and the application of these membranes in PEFC technology, on the other. Indeed, spatially resolved NMR appears to emerge as an important tool in designing and identifying a membrane electrolyte for fuel cell application. Interestingly, a peak power density of 210 mW/cm^2 at a load current-density of 500 mA/cm^2 is achieved for the PEFC with PVA–PSSA membrane compared to a peak power density of only 38 mW/cm^2 at a load current density of 80 mA/cm^2 for the PEFC with pristine PVA membrane while operating at 75 °C with H$_2$ and O$_2$ feeds to the fuel cell maintained at atmospheric pressure.

2. Experimental

2.1. Preparation of PVA–PSSA membranes

PVA (99.7% hydrolyzed, M.W. 115,000, Loba Chemie, India), poly(sodium-poly-styrene sulfonate) (Acros Organics, M.W. 70,000), glutaraldehyde (25% aqueous) and sulfuric acid (98%) (both obtained from S.D. Fine Chemicals, India), and solvents were used as received. De-ionized water (18.4 MΩ cm) used for experiments was produced by a Millipore system.

100 mL of 10 wt.% PVA aqueous solution was prepared by dissolving the preweighed amount of PVA in water at 90 °C followed by its stirring for about 3 h so as to obtain a clear solution. The solution thus obtained was allowed to cool to room temperature. 2 mL of glutaraldehyde (GA) solution was added gradually followed by its stirring for 3–4 h. The required amount of poly(sodium-poly-styrene sulfonate) dissolved in water was added to the resultant PVA solution. The resultant mixture was stirred at room temperature till homogeneous slurry was obtained. The resulting slurry was referred to as PVA–PSSA solution. The slurry was then cast as a membrane on a flat Plexiglass plate and allowed to dry at 60 °C in a forced convection air oven. PVA and PVA–PSSA blend membranes thus formed were removed and dipped in 2 M aqueous H$_2$SO$_4$ solution for 3 h at room temperature (∼30 °C) to exchange Na$^+$ ions with H$^+$ ions. This procedure precludes the presence of Na$^+$ ions in the PVA–PSSA blend membrane. This process is also desired for the subsequent chemical cross-linking of the blend membrane as evidenced from membrane insolubility in water. After the reaction, the membranes were taken out and washed copiously with deionized water to expel residual H$_2$SO$_4$. All the membranes were stored in water for later use. The thickness of all the resultant membranes were around 150 μm.

2.2. Proton conductivity measurements on PVA–PSSA membranes

Proton conductivity measurements were performed on the membranes in a typical two-electrode cell by ac impedance technique. The conductivity cell composed of two stainless steel electrodes each of 20 mm diameter. The membrane sample was sandwiched between the two stainless-steel electrodes fixed in a Teflon block and kept in a closed glass container. Desired RH values in the test chamber were maintained using salt solutions as described in Ref. [22]. In brief, to obtain 100% RH, de-ionized water was used; saturated (NH$_4$)$_2$ SO$_4$ was used to produce 80% RH; saturated NaNO$_2$ was used to produce 65% RH; saturated CaCl$_2$ was used to produce 30% RH, and for 0% RH, solid P$_2$O$_5$ was kept at the bottom of the closed container for 10 h in each cases. The a c impedance spectra of the membranes were recorded in the frequency range between 1 MHz and 10 Hz with amplitude of 10 mV using Autolab PGSTAT 30. The resistance value associated with the membrane conductivity was determined from the high frequency intercept of the impedance with the real axis. The membrane conductivity was calculated from the membrane resistance, R, using the following equation:

$$\sigma = \frac{l}{RA} \tag{1}$$

where σ is the proton conductivity of membrane (S/cm), l is the membrane thickness (in cm) and A is the cross-sectional area of the membrane samples (in cm^2).

2.3. Weight loss measurements on PVA–PSSA membranes

Weight losses in PVA and PVA–PSSA blend membranes were obtained by immersing the membrane samples into deionized water at room temperature for 24 h. Subsequently, the membranes were taken out, wiped carefully with a tissue paper, and immediately weighed on a microbalance. After drying the samples overnight in an air oven at different temperatures ranging between 60 and 110 °C, samples were weighed again and the net weight loss that corresponds to the water loss in the membranes, W, was obtained from the expression:

$$W = \frac{W_{wet} - W_{dry}}{W_{dry}} \tag{2}$$

In Eq. (2), W_{dry} and W_{wet} are the weights of dry and corresponding water-sorbed membranes, respectively.

2.4. Thermogravimetric analysis

The degradation process and the thermal stability of the membranes were studied using a SDT Q600 V8.2 TGA Instrument. The measurements were made from 30 to 650 °C at a heating rate of 10 °C/min under N_2 atmosphere.

2.5. Ion-exchange capacity measurements

Ion exchange capacity (IEC) indicates the number of milliequivalents (mequiv.) of ions in 1 g of the dry polymeric membrane. To determine the ion exchange capacity, membranes of similar weight were soaked in 50 mL of 0.01N sodium hydroxide (NaOH) solution for 24 h at ambient temperature [23]. Subsequently, 10 mL of the solution was titrated with 0.01N sulfuric acid (H_2SO_4). IEC was calculated from the following equation:

$$IEC = \frac{(B-P)0.01 \times 5}{m} \qquad (3)$$

where IEC = ion exchange capacity (in mequiv./g), B = amount of sulfuric acid used to neutralize blank sample solution in mL, P = amount of H_2SO_4 used to neutralize the membrane soaked solution used in the study in mL, 0.01 = normality of the H_2SO_4, 5 = the factor corresponding to the ratio of the amount of NaOH used to soak the membrane to the amount used for titration, and m = polymeric membrane mass in g.

2.6. NMR studies on self-diffusion coefficients of water and water releasing kinetics (diffusion of water from membrane ball to heavy water)

The self-diffusion coefficient of water absorbed in membranes was determined by NMR pulsed field gradient stimulated echo (PGSTE) technique [24]. The experiment was carried out on a Bruker 500 MHz wide-bore Avance II NMR system equipped with a 5-mm diffusion probe, permitting maximum z-gradient amplitude of about 18 T m^{-1}. The sample in each case was a piece of the membrane (ca. 4 mm × 4 mm × 150 μm) saturated with water and surface blotted. A set of experiments was carried out separately for PVA, PVA–PSSA (25 wt.%) blend membranes, as well as for Nafion®, all at 25 °C. The relevant experimental parameters were: spectral width = 100,000 Hz; relaxation delay = 5 s; number of time domain data points = 1024; number of scans = 4. The diffusion experiment was performed as a function of gradient amplitude. The fit equation employed to obtain the diffusion coefficient (D) was

$$I(g) = I(0)\exp\left(-D\gamma^2 g^2\delta^2\left(\Delta - \frac{\delta}{3}\right)\right) \qquad (4)$$

where $I(g)$ is the signal intensity that results for a gradient amplitude g, $I(0)$ is the signal intensity that results when the gradient is off, γ is the magnetogyric ratio of the observe nucleus, δ is the gradient pulse duration (1 ms) and Δ is the time interval between the start of the two gradient pulses (5.78–70 ms) that encode and decode the diffusion.

Echo planar imaging based diffusion maps [25] of these membranes (ca. 3 cm × 2 cm × 150 μm) were also generated based on the Pulsed Gradient Spin Echo (PGSE) method [26] at 200 MHz on a Bruker Biospec 47/40 USR system to obtain the apparent diffusion coefficients (ADC's) in chosen regions of interest employing coronal (ZX) images. The experiments were performed with a 112/72 mm resonator in an actively shielded 12 cm gradient insert. ADC's were thus obtained for water using membranes equilibrated in water and surface bloated.

Kinetic studies of water release by the membranes (diffusion of water from membrane balls to surrounding heavy water, D_2O)

were also undertaken on the Bruker Biospec system, operating at 200 MHz. A series of 64 × 64 gradient echo images were acquired as a function of time after the membrane 'ball' equilibrated in water is dropped in D_2O. The first experiment in each case is initiated around 10 m after dropping the water-equilibrated ball in D_2O. The ball diameter ranged from ~5 to 8 mm. The relevant image parameters are: Coronal images, 15° pulse flip angle, echo time TE = 3.57 ms, repetition time TR = 300 ms, FOV = 2.3 cm, slice thickness = 1 mm (4 mm for Nafion®) and number of averages NA = 8.

2.7. Performance evaluation of PVA–PSSA membranes in PEFCs

The membranes were also used for their performance evaluation in H_2/O_2 polymer electrolyte fuel cells by making membrane electrode assemblies (MEAs). Both anode and cathode comprise a backing layer, a gas-diffusion layer and a reaction layer. Teflonised Toray carbon papers (thickness = 0.27 mm) were employed as the backing layers in these electrodes. Diffusion layers comprising 1.5 mg/cm^2 of Vulcan XC-72R carbon slurry dispersed in cyclohexane were applied onto the backing layers and sintered in a muffle furnace at 350 °C for 30 min. In-house prepared 40 wt.% Pt catalyst supported on to Vulcan XC-72R carbon [27] was coated on to the diffusion layers. The catalyst loading on both the anode and the cathode (active area = 25 cm^2) were kept at 0.5 mg/cm^2. A thin layer of PVA solution in case of the MEA of pristine PVA membrane and in the MEA of blend membrane, a thin layer of PVA–PSSA solution of respective composition similar to the composition of PVA–PSSA blend membranes was spread onto the catalyst surface of each electrode. Membrane electrode assembly (MEA) was obtained by hot pressing the cathode and anode sandwiched with the PVA and PVA–PSSA blend membrane at 15 kN (~60 kg/cm^2) at 80 °C for 3 min. MEA performance was evaluated using a conventional 25 cm^2 fuel cell fixture with parallel serpentine flow field machined on graphite plates (Schunk Kohlenstofftechnic). The cell was tested at 75 °C with gaseous hydrogen and oxygen at anode and cathode side respectively at atmospheric pressure. Both the gaseous reactants were passed through humidifiers before feeding them to the cell. The flow rates for both hydrogen and oxygen gases were kept as 1 L/min using mass flow controllers (Aalborg Instruments and Controls, USA). The humidifiers are kept 10 °C higher than the cell temperature. Measurements of cell potential as a function of current density are conducted galvanostatically using an LCN100-36 electronic load from Bitrode Corporation, USA.

3. Results and discussion

3.1. Proton conductivity study

Fig. 1 shows a plot of proton conductivity of pristine PVA and PVA–PSSA blend membranes as a function of RH. The proton conductivity of the pristine PVA membrane in fully humidified condition is 1.3×10^{-3} S/cm at 30 °C. But the conductivity decreases gradually with decrease in RH. At 0% RH, the conductivity of pristine PVA membrane is found to be only ~1.0×10^{-5} S/cm. The proton conductivity of the PVA–PSSA blend membrane increases with increase in PSSA content at all RH values. Under fully humidified condition, a maximum proton conductivity of 1.66×10^{-2} S/cm is exhibited by PVA–PSSA blend membrane. Unlike the pristine PVA membrane, the proton conductivity of PVA–PSSA blend membranes decreases with decrease in RH. However, the conductivity of the blend membrane happens to be higher than the pristine PVA membrane at all RH values. At 30% RH, the maximum conductivity of PVA–PSSA blend membrane is about two orders of magnitude higher than the conductivity values of pristine PVA membrane. Pro-
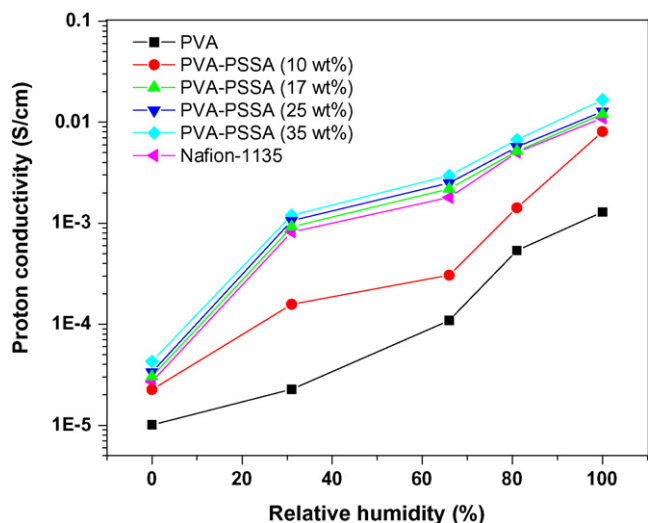
Fig. 1. Variation in proton conductivity for Nafion®, PVA and PVA–PSSA blend membranes as a function of RH.

Fig. 2. Weight loss for water-sorbed PVA and PVA–PSSA blend membrane as a function of temperature.

ton conductivity values for PVA–PSSA blend membrane are nearly similar to those for commercially available Nafion-1135 membrane at all relative humidity values studied here. At lower RH values, due to lack of formation of properly ordered microphase separation, poor conductivity values are observed both for pristine PVA and PVA–PSSA blend membranes.

In general, during the chemical treatment hydroxyl groups of PVA matrix tend to cross-link with glutaraldehyde to generate a hydrophobic barrier providing the polymer a stable morphology that prevents the polymer from dissolving in water. The hydrogen bonds between $-OH$ groups in PVA and $-SO_3H$ groups in PSSA possibly result due to the decreased distance between the two adjoining polymeric chains. This physical interaction between the two functional groups results in the formation of hydrophilic ionic channels (or microdomains) by the arrangement of hydrophilic polymeric groups that facilitate proton conduction [6].

It is noteworthy that the maximum proton conductivity for pristine PVA membrane is observed at 80 °C; subsequently, the conductivity decreases primarily due to the dehydration of the membrane [28]. By contrast, the maximum proton conductivity of PVA–PSSA blend membrane is observed at 100 °C. Accordingly, not only the capacity of water uptake but also the capacity of the membrane to retain water at higher temperatures is seminal for its proton conductivity. This could be explained by the liquid water content in the membranes corresponding to two different types of proton conduction mechanism namely vehicular and Grötthus type.

The aforesaid observation can be visualized by conducting the weight-loss studies for the water saturated PVA and PVA–PSSA blend membrane at various temperatures shown in Fig. 2. It is seen that the weight loss for the PVA membrane is almost negligible after 80 °C. By contrast, appreciable weight loss for PVA–PSSA blend membrane is observed after 80 °C. According to vehicular mechanism [29], water can act as a proton-carrying medium. When water evaporates around 80 °C, the proton conductivity of pristine PVA membrane recedes. On the other hand, PVA–PSSA blend membranes have higher water content than the pristine PVA membrane. We observe the weight loss for the PVA–PSSA blend membrane after 80 °C due to the evaporation of hydrogen-bonded water present between PVA and PSSA moieties in the blend membrane. Thus, at relatively higher temperatures, where lack of water is observed, the proton hoping (Grötthus) mechanism is respon-
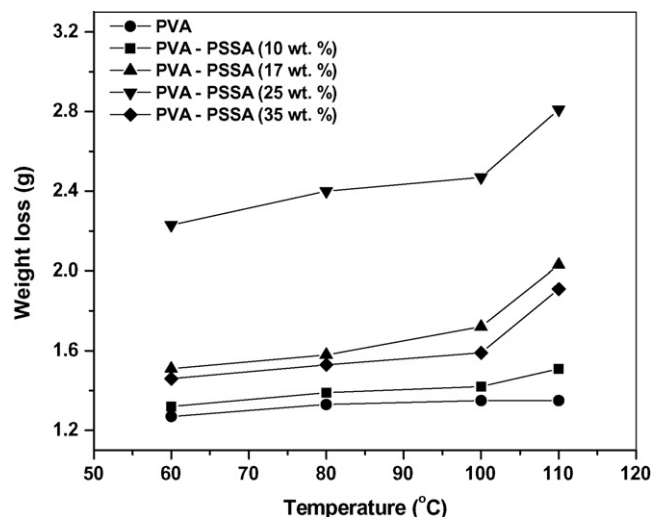
sible for the conductivity. In case of PVA–PSSA blend membranes, the water uptake and weight loss for the membranes are found to increase with PSSA content and reached a maximum value at PVA–PSSA (25 wt.%). In case of PVA–PSSA (35 wt.%) blend membrane the water uptake and weight loss is decreased, may be due to an increase in the degree of cross-linking leading to the reduction of optimum space desired to retain water around sulfonic acid groups.

3.2. Thermogravimetric analysis

As shown in Fig. 3, thermogravimetric analysis (TGA) data for the PVA–PSSA blend membranes are fitted using three main degradation stages, namely thermal dehydration, thermal desulfonation, and thermal oxidation of the polymer matrix. The first weight loss of 30 wt.% between 30 and 180 °C is due to the removal of water from the PVA–PSSA blend membrane while a weight loss of only about 10 wt.% is observed for pristine PVA membrane between 30 and 150 °C. The second weight loss of about 10 wt.% for PVA–PSSA blend membranes is found between 180 and 420 °C, and corresponds to
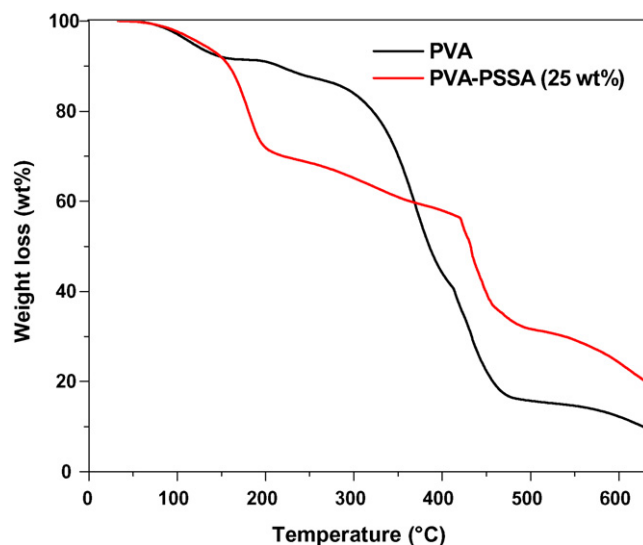

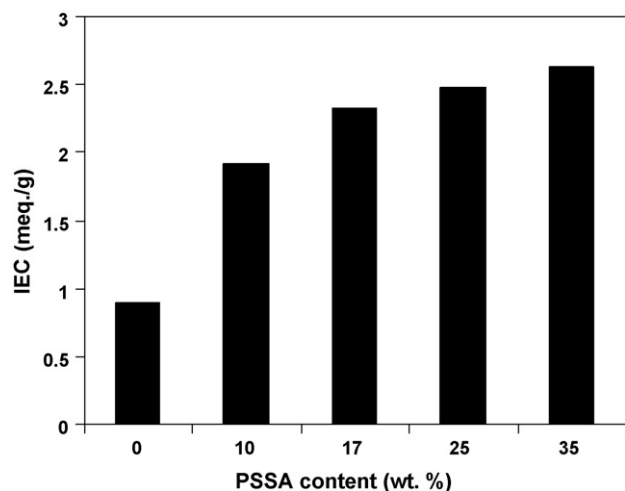**Fig. 3.** TGA thermograms for PVA and PVA–PSSA blend membranes.

Fig. 4. Variation in ion-exchange capacity for Nafion®, PVA, and PVA–PSSA blend membranes.

Fig. 5. Plot of signal intensity *vs. b*, from diffusion weighted images.

loss of sulfonic acid groups by desulfonation; no such weight loss is seen for pristine PVA membrane due to absence of sulfonic acid groups. In the third weight loss region, at temperatures exceeding 420 °C, the polymer residues were further degraded at $T = 470$ °C, which corresponds to the decomposition of the main chains of the PVA [20]. By comparison, PVA membrane undergoes total thermal oxidation between 150 and 470 °C due to the decomposition of its polymeric (side and main) chains. The remnant weight after the polymer decomposition in all the membranes is due to the residual char.

3.3. Ion-exchange capacity

Ion-exchange capacity (IEC) provides an indication, with an indirect and reliable approximation, for the ion exchangeable groups present in a polymer matrix responsible for proton conduction. It is reported that the IEC value for Nafion® 117 is 0.91 mequiv./g [6]. The IEC values for PVA and PVA–PSSA blend membranes studied here are shown in Fig. 4. It can be seen that the IEC values for PVA–PSSA membranes range between 1.921 and 2.625 mequiv./g, and are higher than the IEC value of 0.891 mequiv./g obtained for pristine PVA membrane. IEC values for PVA–PSSA blend membranes suggest these to be a promising alternative to Nafion® membranes.

3.4. Measurement of self-diffusion coefficient by nuclear magnetic resonance

Apparent diffusion coefficients (ADCs) were obtained at 500 MHz and at 200 MHz on membrane samples. The data from diffusion-weighted images run at 200 MHz are presented in Fig. 5 and summarized in Table 1. These data were obtained by a two- or three-parameter fit of the data obtained from six diffusion-weighted images in each case, in accordance with the following equation:

$$I(b) = I(\infty) + (I(0) - I(\infty))\exp(-bD_{app}) \tag{5}$$

In Eq. (5), $I(b)$ is the image intensity for a given value of the diffusion weighting factor b, and other symbols have obvious significance. From Table 1, the close agreement of these image-based values of D_{app} obtained at 200 MHz with the self-diffusion measurement results at 500 MHz [28] may be noted. It is found that the apparent self-diffusion coefficient D_{app} of water in all the membranes is about an order of magnitude less than that of liquid water (2.3×10^{-9} m^2 s^{-1}). D_{app} of water in PVA membrane is lower than that of water in the PVA–PSSA (25 wt.%) blend membrane, while it is highest for Nafion® (6.28×10^{-10} m^2 s^{-1} at $\Delta = 5.78$ ms). It is suggestive to interpret trends in D_{app} in terms of the relative efficiency of the Grötthus mechanism. It may further be noted that our studies of D_{app} as a function of Δ at 500 MHz permit the actual value of D, as well as of the barrier scale to be inferred, employing our general equation [28] when the long time limit ($\Delta \gg a^2/(2D)$) does not obtain:

$$D_{app} = \frac{a^2}{12\Delta}[1 - e^{-\pi^2 D\Delta/a^2}] \tag{6}$$

These measurements indicate that PVA has a distance scale of restriction of 17 μm, PVA–PSSA does not exhibit significant dependence of D_{app} on Δ and the dependence could not be determined for Nafion® owing to large line-widths.

3.5. Kinetic study (diffusion of water from membrane ball to heavy water)

The diffusion of water from Nafion®, PVA and PVA–PSSA (25 wt.%) membrane balls to surrounding D$_2$O [21] was recorded at different time intervals by gradient echo imaging. Some gradient echo images are presented in Fig. 6. The kinetics data are culled from the image analysis, presented in Fig. 7a–c and summarized in Table 2. The equation used for fitting the curve is

$$Y = Y_0 + A_1 \exp\left(\frac{-t}{t_1}\right) \tag{7}$$

Table 1
Apparent diffusion coefficients obtained from diffusion weighted imaging; $\Delta = 5.036$ ms

Membrane specification	Diffusion coefficient ($\times 10^{10}$ m^2/s)
PVA	3.78538
PVA–PSSA (25 wt.%)	4.87271
Nafion®	7.53108

Table 2
Water release kinetics data for PVA, PVA–PSSA and Nafion® membranes

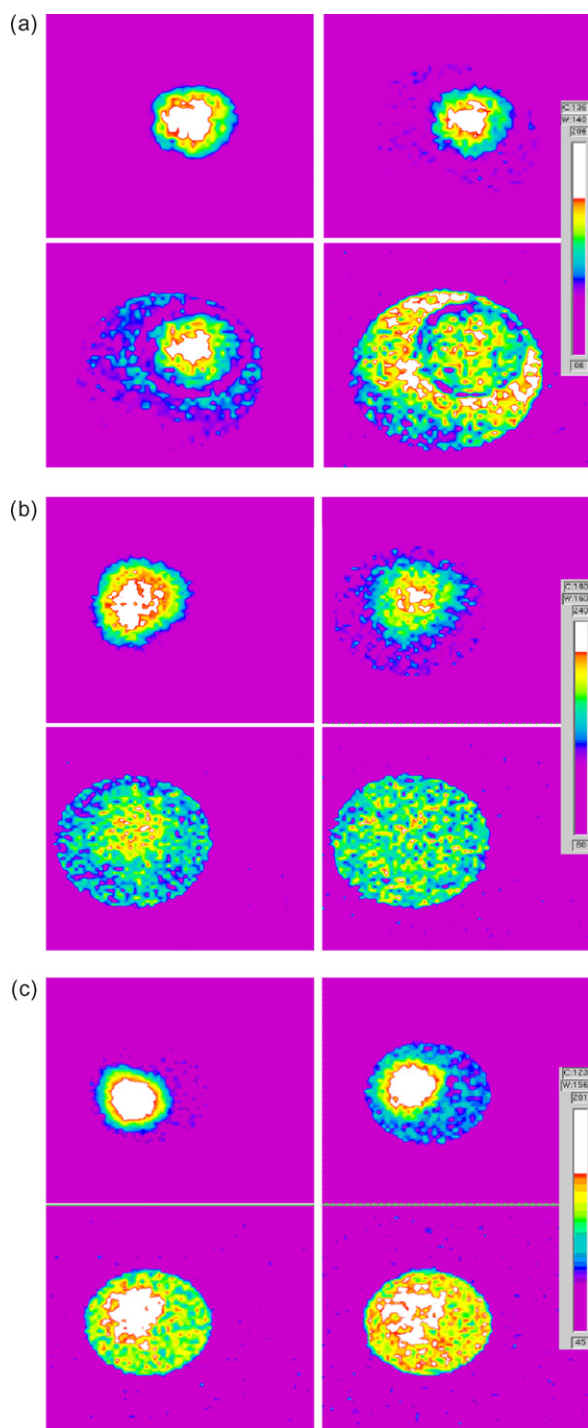| Membrane	Y_0	A_1	t_1 (min)	R^2
PVA	0.77147	1.30174	45.69249	0.99946
PVA–PSSA (25 wt.%)	0.49407	3.06991	9.87492	0.96871
Nafion®	0.19134	1.61503	33.88382	0.99917

Fig. 6. (a) NMR images from left to right, top to bottom: 10, 46, 61, and 135 m after dropping Nafion® ball in D_2O; (b) NMR images from left to right, top to bottom: 10, 56, 107, and 182 m after dropping PVA ball in D_2O; (c) NMR images from left to right, top to bottom: 9, 26, 47, and 99 m after dropping PVA–PSSA ball in D_2O.

Fig. 7. Plot of water release kinetics of (a) Nafion® ball, (b) PVA ball, and (c) PVA–PSSA ball.

The mean intensity of the water signal in a region of interest (ROI) chosen to fully enclose the ball in the first image was plotted as a function of time. It may be noted that while the water self-diffusion coefficients in the three membranes indicate the largest value for Nafion® and the smallest for PVA, the kinetics of water release in these 'ball in D_2O' experiments indicate that the PVA–PSSA (25 wt.%) membrane has the fastest release kinetics and PVA the slowest. This observation could be of relevance under the operating
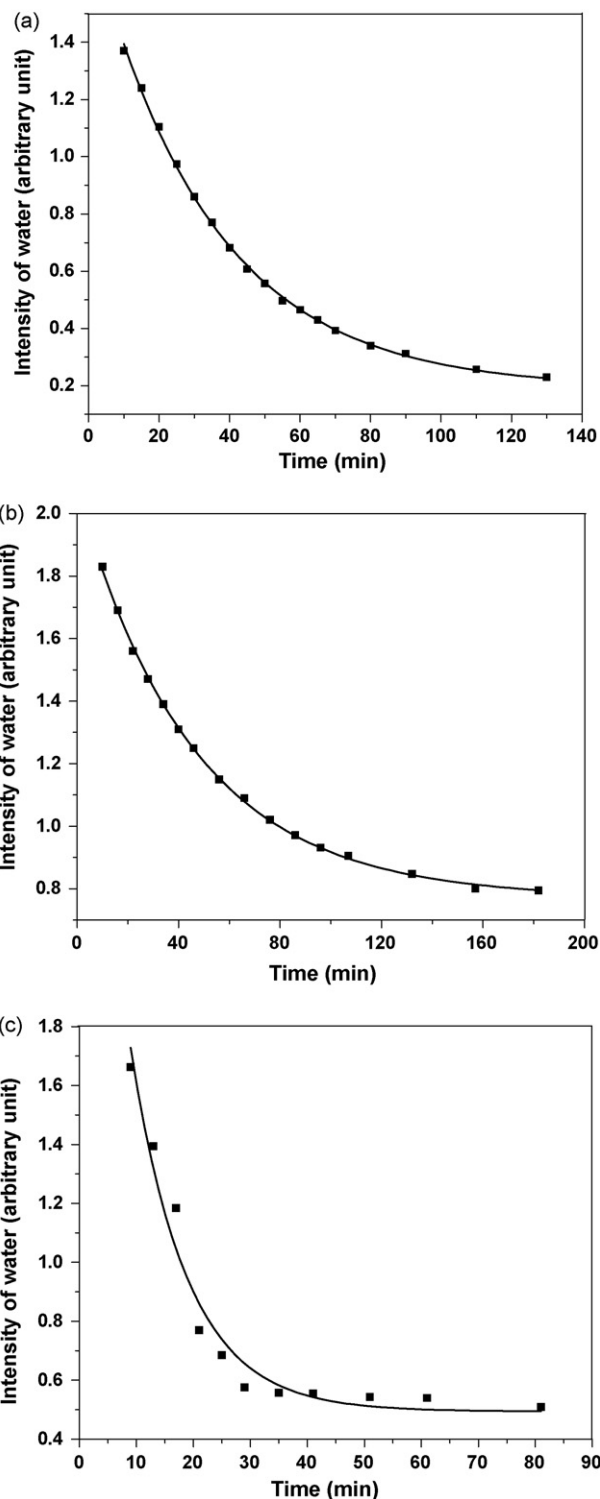
conditions of the fuel cells, especially those with H_2/O_2, since these involve different concentrations of the relevant molecular species across the membrane.

It is interesting to note that PVA based membrane is able to hold more water content as seen by the higher values of intensity of water expressed in arbitrary units (Fig. 7), when normalized to the membrane dry mass. The mass normalized initial water intensities
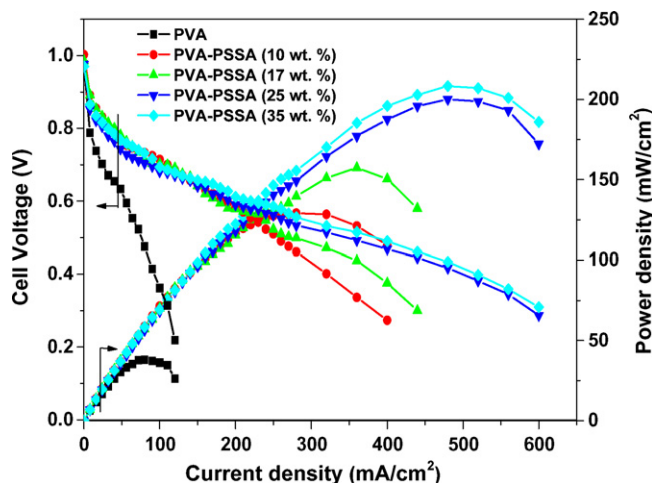
Fig. 8. Performance curves for PEFCs employing PVA and PVA–PSSA blend membranes at 75 °C with gaseous hydrogen and oxygen feed at atmospheric pressure.

correspond to 6 (Nafion®), 13 (PVA) and 53 (PVA–PSSA). This observation is noteworthy and, to our knowledge, first ever of its type reported in the context of water management in fuel cell operation.

3.6. Fuel cell performance evaluation

The performance of the H_2/O_2 PEFC employing PVA and PVA–PSSA blend membranes is studied by obtaining their polarization curves as a function of load current. Fig. 8 compares the polarization curves for all types of membranes under fully wet condition (≈100%RH) at 75 °C. PVA–PSSA blend membranes with varying PSSA content shows better performance than those with pristine PVA membrane. It is apparent from the data in Fig. 8 that the resistance values of the cells with PVA–PSSA blend membranes are lower as compared to that with PVA membrane. The peak power density of 210 mW/cm^2 for the PEFC is achieved with PVA–PSSA (25 wt.%) blend membrane as compared to a peak power density of 38 mW/cm^2 for the PEFC with pure PVA membrane under identical operating conditions.

Proton conductivity in PVA–PSSA blend membranes is attributed to proton transfer through hydrogen bonding with water-filled ion pores. However, an excess of the PSSA could degrade the component not properly cross-linked with glutaraldehyde. Therefore, in this study, the maximum PSSA content is limited to 35 wt.%. It is also apparent from the polarization curves that the early mass-transfer problem observed for PVA membrane is mitigated for PVA–PSSA blend membranes and high load current density is sustained for the PEFC with PVA–PSSA membranes.

In practice, the PVA membrane described above may encounter large interfacial resistance owing to the poor adhesion between PVA film and catalyzed electrodes, resulting in a poor cell performance. However, SEM studies [28] indicate that the membrane surface roughness in blend membranes helps increasing the adhesion and three-phase contact between electrodes and the membrane resulting in improved cell performance. Good mechanical strength and higher single glass-transition temperature for PVA–PSSA blend membrane [28] are attractive merits for the homogeneous and compatible single-phase blend membrane. Although the PEFC comprising PVA–PSSA blend membrane delivers low power density value than that employing the commercial available Nafion® membrane, PVA–PSSA blend membranes would be much cheaper (at least 50 times) than the commercial Nafion® membranes.

4. Conclusions

Novel chemically cross-linked proton conducting PVA–PSSA blend polymer electrolyte membranes with varying PSSA content have been prepared and examined for their proton conductivity and water dynamic property. Interestingly, the PVA–PSSA membrane exhibits higher water uptake and release characteristics in relation to both pristine PVA and Nafion® membranes, as evidenced by NMR imaging technique. The maximum proton conductivity of 1.66×10^{-2} S/cm is observed for PVA–PSSA membrane at 100% RH which is much higher than the conductivity value of 1.33×10^{-3} S/cm observed for pristine PVA membrane. PVA–PSSA membranes are also attractive as a cost-effective option for use in PEFCs.

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