

Preparation of radiochemically pore-filled polymer electrolyte membranes for direct methanol fuel cells

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Abstract

Polymer electrolyte pore-filled membranes, for possible use in direct methanol fuel cells (DMFCs), have been prepared by radiochemical grafting of styrene into porous poly(vinylidene fluoride) (PVDF) films using simultaneous irradiation with an electron beam (EB) followed by a sulfonation reaction. The physico-chemical properties of the obtained polystyrene sulfonic acid pore-filled membranes are evaluated using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), ac impedance, and a methanol diffusion cell. The effects of variation of the grafting yield ($Y\%$) on the ionic conductivity and the methanol permeability of the membranes are investigated. The ionic conductivity of the membranes increases with increase in $Y\%$ and exceeds that of the perfluorinated ionomer membrane, Nafion 117, at a grafting yield of 46%. The methanol permeability of 40 and 46% pore-filled membranes is lower than that of Nafion 117 by 53 and 71%, respectively. The performance characteristic factor suggests that these membranes are potential candidates for DMFC applications.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates for the next generation of power sources required in mobile applications and portable electronic devices [1]. Although pure hydrogen is the preferred fuel for such cells, difficulties remain with its safe storage, transport, and handling in lightweight systems [2]. Liquid hydrocarbons such as alcohol, gasoline and diesel, as well as compressed gases such as butane have been proposed as alternative fuels after being reformed [3]. The inclusion of a reformer does, however, add to system weight, complexity, and cost [4].

The direct methanol fuel cell (DMFC) has potential to eliminate such problems, as it is lightweight and requires no reformer. An aqueous solution of methanol (fuel) is directly fed at the anode where it is oxidized to produce electricity and hydrogen ions. Present DMFC technology uses Nafion 117 membranes to conduct protons from the anode to the cathode and also act as separator. The performance of DMFCs in terms of current density is less than desired due to waste of fuel caused by methanol cross-over such that methanol is oxidized at the cathode and causes a reduction in cell efficiency [5]. In addition, Nafion membranes, which have a fully fluorinated structure are currently expensive [6]. Therefore, new proton-conducting membranes that can offer improvements with respect to reduction of methanol permeation and enhancement of proton conductivity, together with less cost, are desirable substitutes to improve the performance and the economy of DMFCs.

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Motivated by the desire to develop high quality and cost-effective materials, various research groups worldwide have explored the preparation of proton-conducting membranes using two main approaches. The first approach includes direct sulfonation of non-fluorinated polymer backbones such as polyarylenes to produce sulfonated polymers. Typical examples are sulfonated polystyrene (PS) [7], polyphosphazene [8], polyphenylene oxide [9], polysulfone [10], polyether sulfone [11], polyether ether ketone [12], and polyimides [13]. The second approach includes sulfonation of pendent aromatic rings attached to a variety of polymer films that are obtained by radiochemical grafting [14–18] or chemical grafting [6,19] of styrene onto fluorinated polymer matrices. In particular, membranes prepared by radiochemical grafting of styrene on to poly(vinylidene fluoride) films (PVDF) followed by sulfonation have recently attracted great interest after demonstrating superior performance in DMFCs [20]. These membranes were prepared by a pre-irradiation method with an electron beam (EB) based on dense PVDF films as starting matrices [20]. It must be pointed out, however, that no attempt was made to exploit the preparation of sulfonated polystyrene-grafted PVDF using a simultaneous irradiation method with EB. More details concerning the latest developments in radiochemically grafted sulfonated polystyrene membranes based on various fluorinated and partially fluorinated polymer films and their potential applications in PEMFCs and DMFCs can be found in [21].

In recent studies, pore filling of porous substrates with polymer electrolyte has been reported to be an attractive approach to prepare alternative ionomeric membranes known as ‘polymer electrolyte pore-filled membranes’ for DMFCs after their successful introduction for separation of organic liquids by pervaporation [22,23]. In these membranes, the porous substrate acts as an inert ‘rigid’ host that constrains the swelling of the anchored polymer electrolyte and provides the membranes with high-mechanical strength [24]. Pore-filled membranes have been reported to be prepared by a variety of grafting techniques that include chemical grafting [22], photografting [24–26], plasma grafting [27–29], thermal grafting [30], and radiation grafting with γ -rays [31]. By contrast, reports of the preparation of pore-filled membranes using EB can be barely found.

The main aim of this work is to produce polystyrene sulfonic acid (PSSA) pore-filled PVDF membranes using radiation-induced grafting with simultaneous irradiation method with an EB. This method is believed to be useful in simplifying membrane preparation, reducing monomer consumption and homopolymer formation, along with a possible reduction in the cost of the membrane. Styrene was loaded into the PVDF porous matrix, and then grafted under selected reaction parameters. The resulting polystyrene pore-filled PVDF films were subsequently sulfonated under controlled conditions. Some physical and chemical properties, including ionic conductivity and methanol permeability, of the membranes are evaluated with respect to grafting yield ($Y\%$), i.e.,

the content of PS in the pores. Commercial Nafion 117 membrane is used for comparison.

2. Experimental

2.1. Materials

Porous, hydrophobic PVDF films supplied by Millipore under the trade name ‘GVHP’ were used as substrates for the pore-filled membranes. The physical characteristics of these porous PVDF films, as specified by the supplier and as determined elsewhere [32], are presented in Table 1. Styrene of purity more than 99% and chlorosulfonic acid (AR grade) were purchased from Fluka. All the other solvents were also research grade and used without further purification.

2.2. Membrane preparation

Styrene is polymerized into the pores of PVDF films using a simultaneous irradiation method. The porous PVDF films were loaded with styrene by rinsing in a monomer for 24 h prior to the grafting reaction. The excess of monomer was removed by wiping the film surfaces with tissue papers. The styrene-loaded films were quickly placed in thin polyethylene bags, which were filled with purified nitrogen gas and thermally sealed. The bags were then irradiated by an universal electron beam accelerator (NHV-Nissin High Voltage, EPS 3000, Cockroft Walton type, Japan) in which they were placed on a tray moving on a conveyer and subjected to electrons at ambient temperature on a stepwise basis. The conveyer speed was kept constant at 1.45 m min^{-1} . An acceleration voltage of 0.5 MV was used with a current of 1.0 mA to obtain an irradiation dose of 5 kGy per pass. The applied doses were varied from 5 to 50 kGy by increasing the number of passes. The irradiation time was varied in the range of 0.8–8.0 min. After completion of the grafting, the films were rinsed overnight in toluene at 50°C and ultrasonically extracted. The extraction process was repeated a few times to ensure no homopolymer was left in the grafted samples. The grafting yield of polystyrene in pores ($Y\%$) was calculated from:

$$Y\% = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_1 are the weights of PVDF films before and after filling with polystyrene, respectively. The PS pore-filled PVDF films were sulfonated using a mixture composed

Table 1
Physical characteristics of commercial porous PVDF films

Properties	Given values by millipore	Measured values ^a
Porosity (%)	75.0	70.1
Average pore size (μm)	0.22	0.28
Thickness (μm)	110	117.7

^a Stated in reference [32].

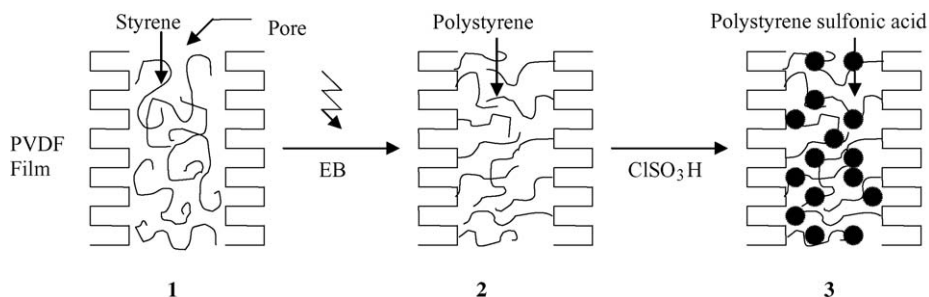


Fig. 1. Schematic representation of pore filling of porous PVDF films with PSSA using simultaneous EB irradiation-induced grafting of styrene and subsequent sulfonation. (1) Loading of styrene in the porous structure of PVDF film. (2) Grafting of styrene to form polystyrene pore-filled PVDF film using EB. (3) Sulfonation of the polystyrene grafted in pores of PVDF films.

of 10% sulfonic acid in dichloromethane for a period of 12 h at room temperature and under a N₂ atmosphere. The resulting membranes, i.e., polystyrene sulfonic acid (PSSA) pore-filled PVDF, were removed and rinsed several times with dichloromethane and deionized water to remove excess chlorosulfonic acid. The membranes were then hydrolyzed with 0.5 M KOH solution overnight and regenerated by boiling with 1 M HCl for several hours. The membranes were then washed with deionized water several times to ensure complete removal of acid, and finally stored in sealed bottles at ambient temperature. A schematic representation for the pore filling of a porous PVDF film with polystyrene sulfonic acid using simultaneous irradiation grafting of styrene with EB and subsequent sulfonation is shown in Fig. 1.

2.3. Membrane characterization

The thickness of PS pore-filled PVDF films and the corresponding PSSA pore-filled PVDF membranes was measured at several points with a digital micrometer (Mitutoyo, Japan).

The porosity of PS pore-filled PVDF films, defined as the volume of the pores divided by the total volume of the porous film, was determined prior to sulfonation by equilibrating in water for 24 h in a closed container. The porosity was determined gravimetrically from the difference in the weights and volumes of the dried samples and their wet counterparts.

Fourier transform infrared (FTIR) measurements were carried out with a Nicolet (Magna-IR 560) spectrometer equipped with attenuated total reflection (ATR, Thunder dome-HATR) having a Ge spherical crystal. The spectra were measured in transmittance mode over a wave number range of 4000–700 cm⁻¹.

Scanning electron microscope (SEM) investigations were conducted with a Philips 505 M microscope. Dry membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, and sputter-coated with thin gold film prior to SEM observation.

The liquid sorption of the membranes was determined by soaking the membrane samples in deionized water or pure methanol for 24 h in a closed container until swelling equilibrium was achieved. Samples were removed and the excess

liquid adhering to the surfaces was quickly removed with tissue papers.

The conductivity of the membranes in acid form was measured by a two-electrode ac impedance technique using a PGSTAT30 frequency response analyzer (Eco Chemie B.V.). Impedance spectra were recorded over the frequency range of 0.1 Hz to 1 MHz. Samples were equilibrated in deionized water for 24 h at room temperature prior to testing. A self-made conductivity cell comprised two stainless-steel electrodes with gold-coated round-end discs of 2 cm diameter was used to host the samples. Prior to any measurement, the surface water was removed, and then the swollen membrane was rapidly placed between the electrodes in the conductivity cell. The water content of the membrane was assumed to remain constant during the short period of time required for the measurement. Impedance data were fitted using the equivalent circuit shown in Fig. 2 by GPES software. The membrane resistance (R) was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end.

Methanol permeability measurements were carried out using a home-made, glass, diffusion cell that consisted of two cylindrical glass compartments (A for feed and B for permeate) separated by a membrane with an effective area of 7.1 cm². A schematic representation of the methanol diffusion cell is presented in Fig. 3. Compartment A was filled with 15 wt.% methanol ($V_A = 55$ ml) and compartment B with deionized water ($V_B = 50$ ml). Both the feed and the permeate solutions were kept under continuous stirring conditions by magnetic stirrers. To determine the methanol permeability of

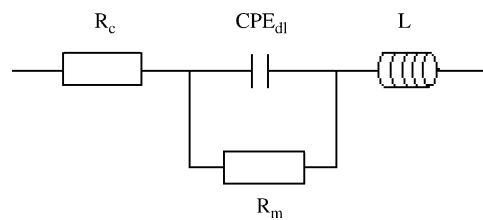


Fig. 2. Equivalent circuit consisting of contact resistance (R_c), a constant phase element for double-layer (CPE_{dl}), membrane resistance (R_m), and inductor (L) representing the influence of connecting cables.

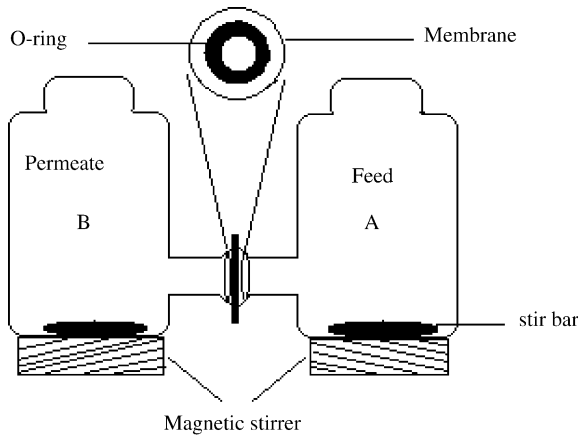


Fig. 3. Schematic representation of methanol glass diffusion cell.

each membrane, liquid samples of 100 μl were taken from the permeate using a syringe at prescribed time intervals. The liquid samples were analyzed with a calibrated gas chromatograph (HP 5890, Hewlett-Packard, USA) equipped with a capillary column (14% cyano propyl phenyl methyl poly siloxane, 30 m \times 0.25 mm \times 1.0 μm) and a flame ionization detector (FID).

Nafion 117 membrane was activated using the procedure provided by du Pont and subjected to various characterization techniques under the same experimental conditions used for PSSA pore-filled PVDF membranes.

3. Theoretical

3.1. Swelling and porosity calculations

The liquid (water or methanol) sorption (S) of PSSA pore-filled PVDF membranes was calculated using the following expression:

$$S = \frac{m_W - m_D}{m_D} \times 100 \quad (2)$$

where m_W is the mass of the swollen membrane and m_D is the mass of the dry membrane.

The porosity (ε) of PS pore-filled PVDF (grafted) films was calculated via:

$$\varepsilon = \frac{(m_W - m_D)\rho_o}{(m_W - m_D)\rho_o + m_D\rho_{\text{H}_2\text{O}}} \quad (3)$$

where m_W and m_D are the weights of the water swollen and dry PS pore-filled PVDF films, respectively, $\rho_{\text{H}_2\text{O}}$ the water density, and ρ_o is the apparent density of the dried PS pore-filled PVDF films that was calculated for each sample by taking into account the dimensional changes caused by PS grafting.

3.2. Ionic conductivity calculations

The ionic conductivity (σ) was calculated from the bulk resistance (R), which was obtained from the intercept of the impedance curves with the real-axis at the high-frequency end according to:

$$\sigma = \frac{L}{R} \frac{1}{A} \quad (4)$$

where L is the thickness of the membrane sample and A is the sample cross-sectional surface area.

3.3. Methanol permeability calculations

The methanol permeability (P) was determined for each membrane sample as follows. Methanol diffusion was established across the membrane due to a concentration gradient. The concentration of methanol in the permeate compartment is given by Eq. (5), as stated elsewhere [33].

$$\frac{V_B}{dt} dC_B = A \times \frac{DK}{L} C_A \quad (5)$$

where C_B is the concentration of methanol in the permeate (water) compartment at time t , C_A the concentration of methanol in the feed compartment, A the membrane cross-sectional area, L the membrane thickness, V_B the volume of the water compartment, D the methanol diffusivity, and K is the partition coefficient. Eq. (5) can be solved to give:

$$C_B(t) = \frac{A}{V_B} \times \frac{DK}{L} C_A(t - t_0) \quad (6)$$

where t_0 is the time lag, which is explicitly related to the diffusivity ($t_0 = L^2/6D$).

Since the permeability (P) is defined as the product of the diffusivity of methanol through the membrane (D) and the partition coefficient (K), i.e., $P = DK$, Eq. (6) can be rewritten as:

$$C_B(t) = \frac{A}{V_B} \times \frac{P}{L} C_A(t - t_0) \quad (7)$$

The methanol permeability (P) is calculated from the linear relationship of concentration change of C_B versus time (t) according to the following expression:

$$P = \alpha \times \frac{V_B}{A} \times \frac{L}{C_A} \quad (8)$$

where α is the slope of the linear plot of C_B versus t .

3.4. Calculation of overall membrane performance

Since DMFC application requires membrane quality that attains high-proton conductivity and methanol impermeability, the membrane performance evaluation can be obtained using the following expression [34]:

$$\Phi = \frac{\sigma}{P} \quad (9)$$

where Φ is a parameter that evaluates the overall membrane performance in terms of the ratio of the ionic conductivity (σ) to the methanol permeability (P).

4. Results

4.1. Grafting reaction

Various membrane samples were prepared in this study using the suggested simplified two-step procedure. The porous PVDF films were filled with different contents of PS by varying the irradiation dose at a constant concentration of 100% styrene during the grafting step. The variation of the grafting yield ($Y\%$), i.e., PS content in the pores, with the irradiation dose is shown in Fig. 4. The grafting yield ($Y\%$) increases steeply with increase in the irradiation dose. A grafting yield as high as 46% was achieved in the PVDF porous structure at an irradiation dose of 50 kGy under a N_2 atmosphere at ambient temperature.

4.2. Sulfonation reaction

The ionic sites, i.e., sulfonic acid groups, were introduced to PS grafted in the pores of the PVDF films by sulfonation with chlorosulfonic acid under controlled conditions. The resulting PSSA pore-filled membranes achieve degrees of sulfonation close to 100%, i.e., the ratio of sulfonic acid groups to phenyl groups is approximately equal to unity. Therefore, the membrane properties are discussed with respect to the content of PS anchored in the pores ($Y\%$).

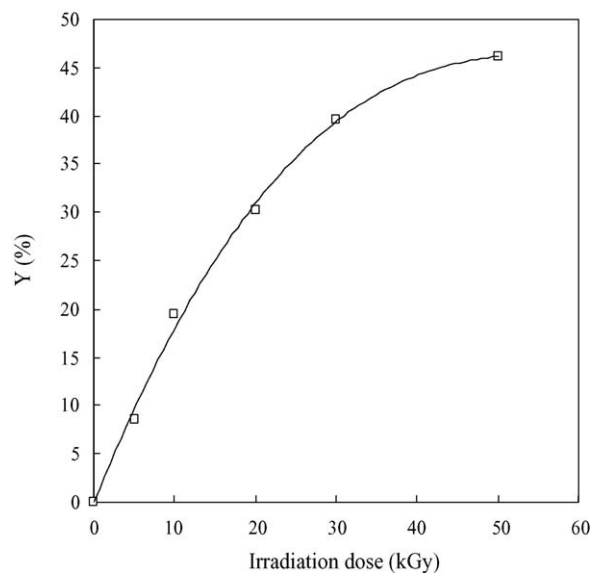


Fig. 4. Variation of the grafting yield with the irradiation dose. Irradiation and grafting conditions are: accelerating voltage, 0.5 MeV; beam current, 1.0 mA; dose per pass, 5 kGy; conveyor speed, 1.45 m/min; temperature, ambient; atmosphere, nitrogen; film thickness, 117.7 μm and no styrene dilution.

4.3. Chemical composition of membranes

The incorporation of polystyrene sulfonic acid in the membranes was verified using FTIR-ATR spectral analysis. Typical spectra of pristine PVDF film, 30% PS pore-filled PVDF film and its corresponding PSSA pore-filled membrane are shown in Fig. 5. Similar spectra were obtained for other membranes with different grafting yields. Grafting of styrene is confirmed by the presence of aromatic ring

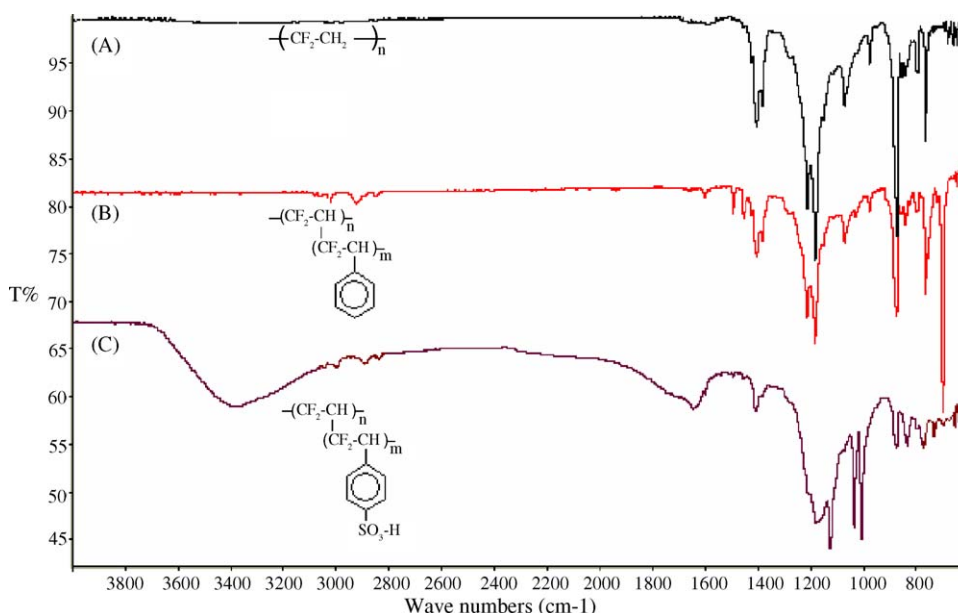


Fig. 5. Typical FTIR spectra of (A) pristine PVDF film, (B) PS pore-filled PVDF film ($Y=30\%$), (C) corresponding PSSA pore-filled PVDF membrane.

features established by the presence of skeletal C=C in plate-stretching vibrations at 1493 and 1602 cm^{-1} , together with C–H aromatic stretching vibrations at 3100–3026 cm^{-1} . A characteristic peak of a mono-substituted benzene ring is also shown at 749 cm^{-1} . Sulfonation of the PS pore-filled PVDF film is confirmed by the presence of the sharp peaks at 1126 and 1007 cm^{-1} , which are due to the introduction of SO_3^- groups. The peak at 1034 cm^{-1} is assigned to the di-substituted benzene rings of PSSA. The broad peak at 3410 cm^{-1} is assigned to the –OH species of water molecules that are involved in hydrogen bonding with the SO_3^- groups.

4.4. Morphology of membranes

The effect of PS grafting and subsequent sulfonation on the morphology of PVDF films in the dry state was investigated. Scanning electron micrographs of the cross-sections of a pristine PVDF film, a 30% PS pore-filled PVDF film and its corresponding PSSA pore-filled membrane are shown in Figs. 6 and 7, respectively. As can be seen, the PS grafts overwhelmingly invade the fibrous microstructure of the PVDF film and convert it into distinctive spherical particles with macroscopic phase separation between them. A small number of intersected pores remain scattered in the structure despite the latter being thickened to a great extent. Sulfonation of the membranes causes further reduction in the remaining pores and converts spherical particles into gel-like clusters (cationic domains) of larger size. The structure of the sulfonated membranes appears uniform with no distinction between the polystyrene sulfonic acid cluster domains and the PVDF matrix.

4.5. Thickness and porosity of grafted films

The measured porosity of a pristine PVDF film is 6.7% smaller than the corresponding value supplied by the manufacturer. This is possibly due to a difference in the method used for porosity measurement. From the thickness measurements, a difference of 7.3% is detected between the given and the measured values. This may be considered to be within experimental error.

Porosity data of PS pore-filled PVDF films determined from Eq. (3) is presented in Table 2 together with the grafting yield ($Y\%$). The porosity of the dry PS pore-filled PVDF films decreases with the increase in $Y\%$ and reaches a minimum

Table 2
Variation of porosity (ε), apparent density (ρ_o), and thickness (L) of PS pore-filled PVDF films with grafting yield ($Y\%$)

$Y\%$	ε (%)	ρ_o (g cm^{-3})	L (μm)
0	70	0.72	117.7
8	43	0.769	125
19	32	1.10	132
30	21	1.27	140
40	12	1.55	146
46	5	1.63	152

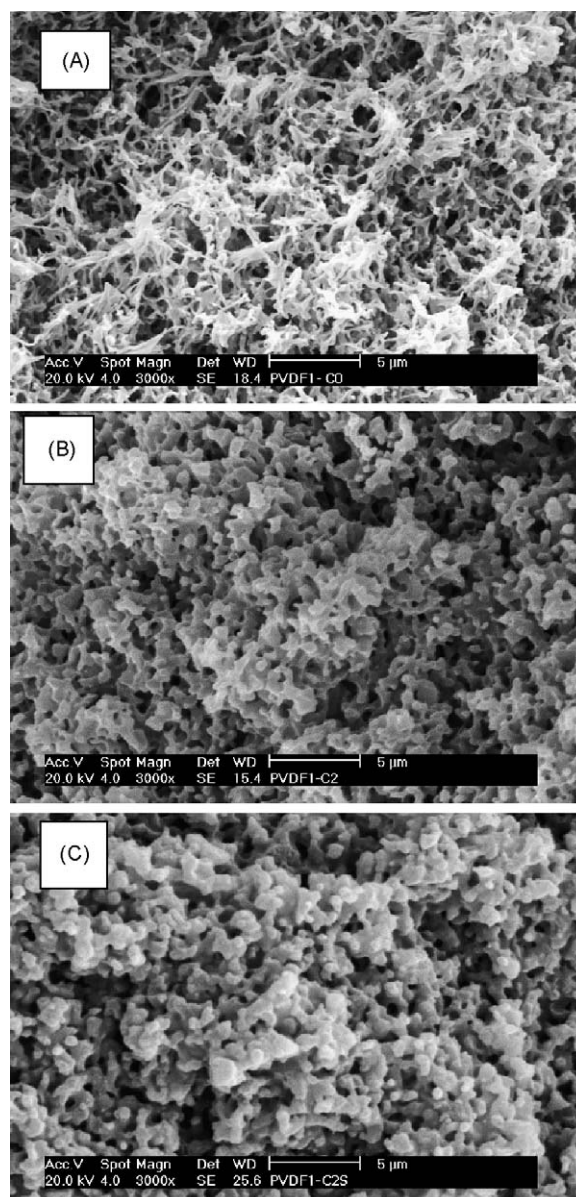


Fig. 6. SEM micrographs of cross-sections of (A) pristine PVDF film, (B) PS pore-filled PVDF film with $Y = 30\%$, and (C) corresponding PSSA pore-filled PVDF membrane (higher magnification).

value of 5% at $Y = 46\%$. This is coupled with a simultaneous increase in both the apparent density of the dry PS pore-filled PVDF films and their thicknesses.

4.6. Swelling behaviour

Variation in the sorption of pure liquids, i.e., water and methanol, as a function of grafting yield ($Y\%$) of PSSA pore-filled PVDF membranes is given in Fig. 8. The sorption of both liquids increases with increase in $Y\%$. Water sorption is higher than that of methanol by more than two folds while the water:methanol sorption ratio remains practically constant (2.3 ± 0.2) with variation in $Y\%$. Moreover, the methanol sorption in these membranes is directly pro-

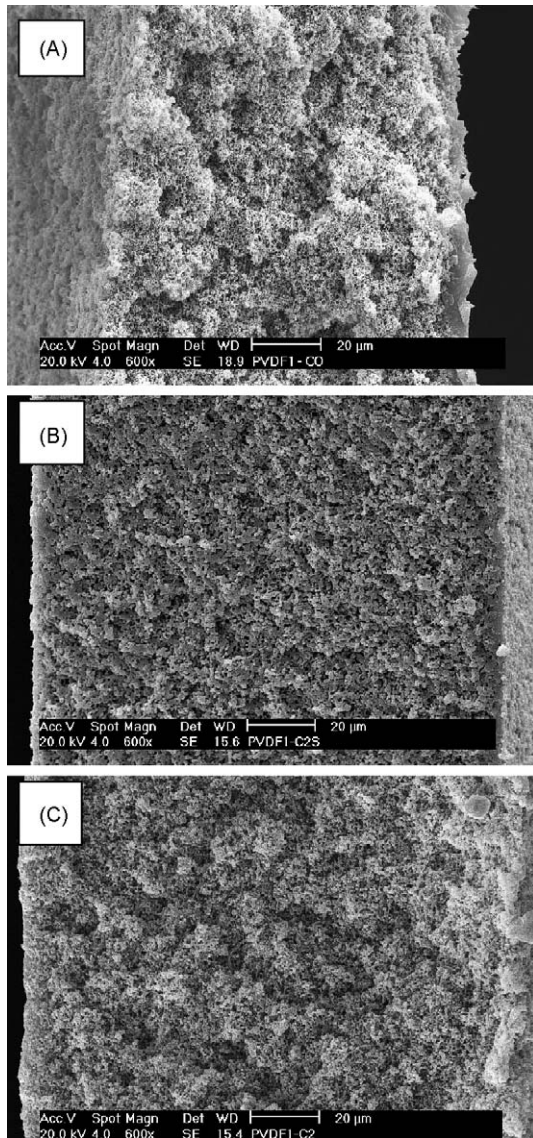


Fig. 7. SEM micrographs of cross-sections of (A) pristine PVDF film, (B) PS pore-filled PVDF film with $Y=30\%$, and (C) corresponding PSSA pore-filled PVDF membrane (lower magnification).

portional to the water sorption, as indicated by the linear relationship presented in Fig. 9. By contrast, Nafion 117 membranes display an inferior water sorption compared with that of methanol and show a water:methanol sorption ratio of 0.46.

4.7. Ionic conductivity

The results of measurements of the ionic conductivity of PSSA pore-filled membranes versus the grafting yield ($Y\%$) are presented in Fig. 10 together with that for a Nafion 117 membrane. The ionic conductivity increases with increase in $Y\%$. Membranes with values of $Y=19\%$ and above record an ionic conductivity as high as $10^{-2} \text{ S cm}^{-1}$. The threshold ionic conductivity value is given by the membrane with $Y=46\%$, viz., $5.8 \times 10^{-2} \text{ S cm}^{-1}$. This ionic conductivity is

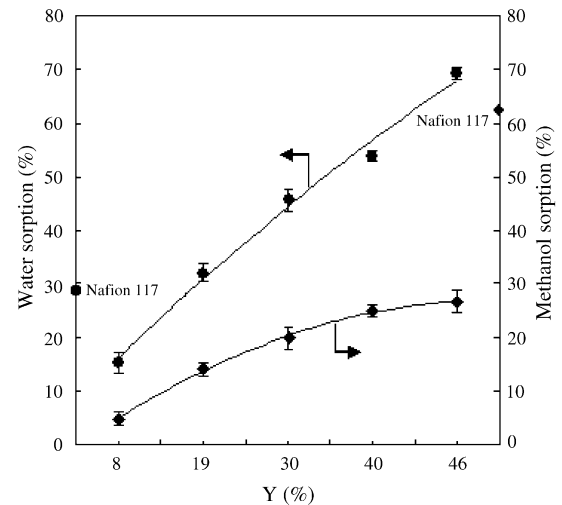


Fig. 8. Variation of water sorption and methanol sorption with grafting yield in PSSA pore-filled PVDF membranes. Nafion 117 is included for comparison.

higher than that of a Nafion 117 membrane, which was found to be $5.3 \times 10^{-2} \text{ S cm}^{-1}$ under the same experimental conditions.

4.8. Methanol permeability

The variation of methanol concentration in the permeate compartment (B) with the time for PSSA pore-filled PVDF membranes with various grafting yields is given in Fig. 11 along with that for a Nafion 117 membrane. All membranes, including Nafion 117, report a linear relationship. The slopes obtained from these linear relationships were used to calculate the methanol permeability according to Eq. (8); the results are listed in Table 3. The methanol permeability of PSSA pore-filled PVDF membranes decreases with the

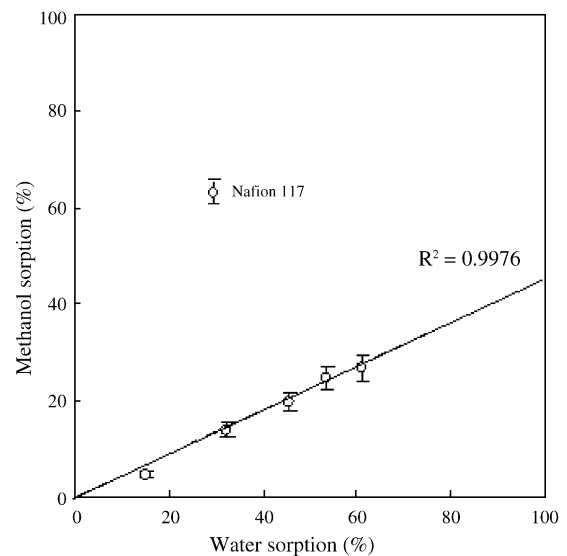


Fig. 9. Methanol sorption vs. water sorption in PSSA pore-filled PVDF membranes with various grafting yields and in Nafion 117.

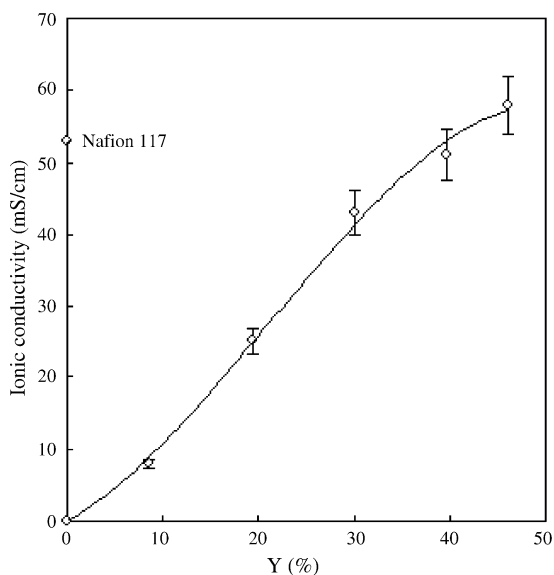


Fig. 10. Variation of ionic conductivity of PSSA pore-filled PVDF membrane with grafting yield. Nafion 117 is included for comparison.

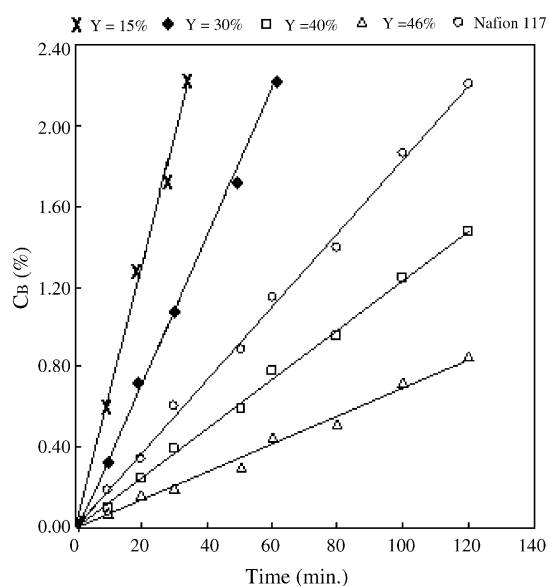


Fig. 11. Variation of methanol concentration in water compartment with time for PSSA pore-filled PVDF membranes with various grafting yields and in Nafion 117 membrane.

Table 3
Variation of methanol permeability of PSSA pore-filled membranes with grafting yield

Y%	Thickness of fully hydrated membranes (μm)	Methanol permeability ($\text{cm}^2 \text{s}^{-1}$)
8	147 ± 2	$2.6 \pm 0.1 \times 10^{-4}$
19	158	1.5×10^{-5}
30	165	4.9×10^{-6}
40	170	1.6×10^{-6}
46	178	1.0×10^{-6}
Nafion 117	223	3.5×10^{-6}

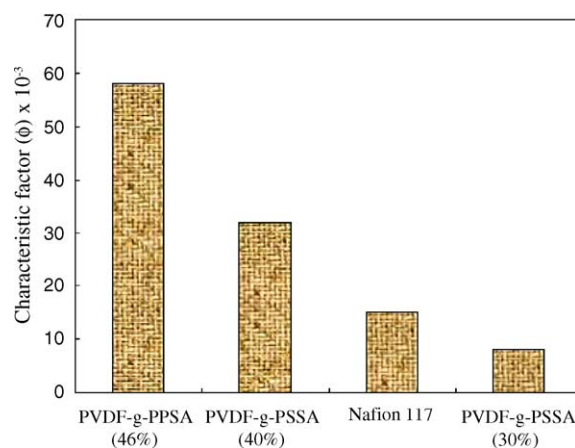


Fig. 12. Comparison of characteristic performance evaluation factor of PSSA pore-filled PVDF membranes with various grafting yields (30, 40 and 46%) and in Nafion 117 membrane.

increase in grafting yield ($Y\%$). Moreover, membranes with $Y=40$ and 46% have a methanol permeability lower than that of a Nafion 117 membrane.

4.9. Overall membrane performance

The overall performance of each membrane, including Nafion 117, was evaluated from Eq. (9). The performance evaluation factor (Φ) for three is PSSA pore-filled PVDF membranes having 30, 40 and 46% grafting yield is compared with that for a Nafion 117 membrane in Fig. 12. The PSSA pore-filled PVDF membranes with grafting yields of 40 and 46% each records Φ (32 and 58, respectively) higher than that for Nafion 117 ($\Phi=15$). By contrast, the Φ of the membrane with a grafting yield of $Y=30\%$ ($\Phi=8$) is lower than that for Nafion by $\sim 40\%$ under the same experimental conditions.

5. Discussion

It has been shown that pore-filled membranes can be successfully prepared by grafting styrene into the porous structure of PVDF films by a simultaneous irradiation technique using EB followed by sulfonation (Fig. 1). Grafting reactions initiated by direct EB irradiation have been performed under controlled parameters that include the irradiation dose to ensure grafting reaches the bulk of the porous PVDF matrix. The EB is operated in the low energy region to reduce the effects of any undesirable side-reactions (e.g., homopolymerization and chain scission) that may hinder the copolymerization of styrene or cause the degradation of PVDF film. The grafting yield ($Y\%$) is strongly dependent on the irradiation dose (Fig. 4). This established behaviour could be attributed to an increase in the number of free radicals that are generated that are in the grafting system. This, in turn, increases the number of styrene molecules that are captured

by the radicals and leads to high-grafting levels in the pores of the PVDF films. Grafting of styrene onto porous PVDF films using EB with a pre-irradiation method has been found to behave similarly [35].

Sulfonation of PS pore-filled PVDF films converts the incorporated PS into polyelectrolyte (PSSA) entrapped inside the porous structure of the PVDF substrate. Degrees of sulfonation (number of moles of sulfonic groups per molecule of styrene) close to 100% are achieved under the present reaction conditions. A similar sulfonation process for PS grafted on dense PVDF films was suggested to be a diffusion-controlled reaction [36]. This means that sulfonation starts at the surface of the grafted layers, and then proceeds towards the internal layers with the diffusion of more sulfonating agent. Considering a constant degree of sulfonation, discussion on the membrane properties reported here is limited to variation in the grafting yield ($Y\%$), i.e., the amount of PS incorporated in the pores of PVDF membranes.

FTIR-ATR spectral analysis has been used to verify the incorporation of a PSSA moiety into the porous structure of the PVDF film and the formation of a polymer electrolyte membrane, as seen in Fig. 5. A comparison between a PSSA pore-filled membrane and its corresponding PS pore-filled PVDF and a pristine PVDF film clearly shows that the PVDF film is grafted with PS, as revealed by benzene ring features and mono-substitution identified by a band at 749 cm^{-1} . This band almost vanishes on sulfonation (confirmed by sharp bands of SO_3^- at 1007 and 1126 cm^{-1}) with the appearance of a di-substituted benzene ring peak at 1034 cm^{-1} . This confirms a degree of sulfonation close to 100%. The strongly hydrophilic nature of these membranes is reflected by the obvious shift in the wave number of the $-\text{OH}$ peak from 3300 to 3410 cm^{-1} under the influence of hydrogen bonding formed between SO_3^- groups and water molecules.

The morphology of the cross-sections of PSSA pore-filled membrane and its corresponding PS pore-filled PVDF film and pristine PVDF film shown in Fig. 6 confirms that grafting of PS already takes place in the pores of PVDF films. The emergence of a new phase structure comprised of spherical particles is most likely due to the aggregation of PVDF and polystyrene. Growth in the size of spherical particles towards gel-like clusters is attributed to the introduction of sulfonic acid groups, which have a strongly hydrophilic nature. The increase in the thickness of the final membrane compared with its corresponding PS pore-filled and PVDF films before grafting (shown in Fig. 7) is yet another indication of the morphological changes that accompany the process of pore filling and subsequent sulfonation.

Investigation of the porosity and the other physical properties has been performed to monitor the progress in pore filling with increase in the grafting yield. The data presented in Table 2 shows that a decrease in the porosity of the PS pore-filled PVDF films, which is accompanied by a simultaneous increase in their apparent densities and thicknesses, is due to a continuous rise in the pore-filled ratio in PVDF matrix. The minimum porosity value (5%) obtained at $Y=46\%$ indicates

that most of the porous structure of the PVDF film is plugged with PS.

The swelling behaviour of PSSA pore-filled PVDF membranes is dependent on $Y\%$, as shown in Fig. 8. The increase in both pure water and methanol sorption with increase in $Y\%$ can be attributed to an increase in the incorporation of strongly hydrophilic sulfonic acid groups. On the other hand, the remarkable increase in the sorption of water at all grafting levels compared with that of methanol indicates that these membranes have preferential sorption for water over methanol. This is confirmed by the water:methanol ratio, which is found to be above unity (2.3 ± 0.2) although it does not significantly vary with increase in $Y\%$. Accordingly, it can be stated that PSSA pore-filled PVDF membranes have higher interactions towards water compared with methanol and the sorption of both liquids is limited to the hydrophilic PSSA domains in the membranes.

The linear correlation between water sorption and methanol sorption presented in Fig. 9 suggests that the remaining pores of the membranes have no difference in the sorption selectivity for water and methanol. Unexpectedly, the Nafion 117 membrane exhibits a methanol sorption (63%) that is higher than that of water (29%) with a water:methanol ratio less than unity (0.46); such values agree very well with data reported in the literature [34,37]. It can be concluded that PSSA pore-filled PVDF membranes prepared in this study have a much less methanol sorption selectivity than Nafion 117 membrane. Similar behaviour has been reported for radiation-grafted membranes based on dense ethylene-tetrafluoroethylene copolymer (ETFE) films that contain polystyrene sulfonic acid moieties [34]. It is interesting to note that the observed water sorption at its highest value (68% at $Y=46\%$) is lower than that of bulk polystyrene sulfonic acid, viz., $\sim 98\%$ [38]. This is most likely due to suppression of swelling by the presence of the porous hydrophobic structure of PVDF substrate.

The dependence of the ionic conductivity of PSSA pore-filled PVDF membranes on the grafting yield ($Y\%$) presented in Fig. 10 is probably caused by the increase in both sulfonic acid groups associated with pore filling and the amount of the sorbed water. This indicates that the incorporation of more PSSA provides a better environment for ionic mobility in these polymer electrolytes. Since there is a relation between the water sorption and the ionic conductivity based on the concept of ionic domain percolation, the high-ionic conductivity demonstrated by these membranes at high-grafting yields, i.e., $Y=40$ and 46% , suggests that the water swollen ionic domains in the membranes pores are inter-connected to form a network structure. Therefore, the lower ionic conductivity observed for membranes with low grafting yields such as 8 and 19% is due to a diffusion limitation caused by segregation in the ionic domains. As the grafting yield increases to a sufficient level (30%), the ionic domains become more inter-connected and reach a percolation threshold beyond which diffusion limitations are overcome and allow the ionic conductivity to reach a maximum value.

A methanol permeability test was performed to evaluate the potential application of PSSA pore-filled PVDF membranes in DMFCs. The lower methanol permeability demonstrated by PSSA pore-filled PVDF membranes particularly at $Y=40$ and 46% compared with Nafion 117 (53 and 71% of that of Nafion 117, respectively) indicates that a significant reduction in methanol cross-over can be achieved using the membranes developed in this work. This can be ascribed mainly to the lower methanol sorption in PSSA pore-filled PVDF membranes compared with that of Nafion 117 (Fig. 10). From Table 3, it is obvious that the increase of methanol sorption with PSSA content leads to a decrease in methanol permeability. Similar radiation-grafted membranes, prepared by a γ -radiation-induced grafting method ($Y=34$ and 42%) and based on dense ETFE films containing PSSA moieties, exhibited lower methanol permeability than a Nafion 117 membrane [34].

The performance evaluation factor (Φ) for PSSA pore-filled PVDF membranes with grafting yields of 40 and 46% is higher than that of a Nafion 117 membrane. This is considered to be attractive for application in DMFCs. The decrease in methanol permeability in the presence of high-ionic conductivity is expected to improve the cell efficiency and the power density [39].

6. Conclusions

Polystyrene sulfonic acid pore-filled membranes have been prepared using a simultaneous EB irradiation grafting method. Styrene is grafted into the pores of PVDF films and the polystyrene pore-filled films are then sulfonated. Use of this method is found to simplify the pore filling process and reduce the reaction time, as well as the monomer consumption.

The grafting yield (amount of polystyrene anchored in the pores) is found to be a function of the irradiation dose. FTIR and SEM results confirm the grafting and sulfonation of PVDF films. The membranes have a strong hydrophilic character that is caused by the incorporation of sulfonic acid groups. The ionic conductivity is a function of the grafting yield. Membranes with a grafting yield as high as 46% display higher ionic conductivity and lower methanol permeability than a Nafion 117 membrane.

The overall findings suggest that some of the pore-filled PVDF membranes offer potential for improving the performance of DMFCs, provided that they possess adequate stability. Further research work is undergoing to cross-link these membranes and test their performance in DMFCs and address their stability issues.

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