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Physico-chemical study of sulfonated polystyrene pore-filled electrolyte membranes by electrons induced grafting

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Abstract

Pore-filled polymer electrolyte membranes have been prepared as a potential proton exchange membrane by radiation induced grafting using simultaneous technique. The porous substrate films were grafted in a subsequent step after flooding the membranes pores with styrene monomer. The grafted films were then sulfonated in a post-grafting reactions. The influence of grafting conditions, i.e. irradiation dose and monomer concentration in correlation with the grafting yield (Y) have been investigated. The results showed that the grafting yield is increased for both conditions. The resulting membranes were then characterized by evaluating their physico-chemical properties such as ion exchange capacity, water uptake and proton conductivity as a function of grafting yield. The overall results showed that polystyrene grafts is successfully anchored within the pores of PTFE films during grafting and subsequently transformed into hygroscopic proton exchange regions after being sulfonated. The measured conductivity of the sulfonated polystyrene pore-filled electrolyte PTFE membranes achieved were approximately within the magnitude of 10^{-3} and $10^{-2}\,\mathrm{S\,cm^{-1}}$ at room temperature and at higher operating temperature, respectively.
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1. Introduction

Membranes with high proton conductivity are potentially useful as separators and electrolytes in electrochemical cells such as batteries and fuel cells. Over the past decade, studies of proton exchange membranes (PEMs) for polymer electrolyte fuel cell have focused especially on perfluorosulfonic acid membranes such as Nafion (DuPont), Dow (DOW Chemicals) and Flemion (Asahi Glass) [1,2]. This is because they exhibited a number of desirable properties, namely high ionic conductivity, mechanical strength, chemical/thermal stability and reasonably low water swelling [2,3]. The high material prices, electro-osmotic water flows and methanol crossover rates in these materials, however, are undesirable for fuel cell applications [4]. These circumstances stimulate a research into alternative PEM materials, which can overcome the abovementioned problems that can be produced economically.

A new concept of ion exchange membranes has been developed in which a controlled amount of polyelectrolyte was anchored within the pores of a porous membrane [5]. The general principle behind this new concept of a pore-filled electrolyte membrane is predicted on combining the most desirable properties of two materials, which are a porous substrate and a polymer that fill the pores of the base substrates. The porous support in these membranes functions as an inert "rigid" host or shell that constrains the polyelectrolyte, and limiting its swelling, thus provides mechanical strength for the membrane.

Hence, in this study, we report the work done on the preparation of sulfonated polystyrene pore-filled electrolyte PTFE membranes by using electron radiation grafting method and sulfonation of the pore-filled films. The physico-chemical properties of the sulfonated polystyrene pore-filled electrolyte PTFE membranes such as swelling behavior, ion exchange capacity and ionic conductivity were also investigated in correlation with the grafting yield.

2. Experimental

2.1. Materials

The porous substrate used in this study was polytetrafluoroethylene (PTFE) film and prepared by sintering technique [6]. The film had a thickness of 150 μm, average pore size of 0.15 μm and density of 1.94 g/cm^3. Styrene of purity more than 99% (Fluka) was used as the grafting monomer without any further purification. Dichloromethane (JT Bakers), acetone (JT Bakers), toluene (JT Bakers), methanol (Fluka), tetrahydrofuran (Merck), chlorosulfonic acid (Merck) and 1,1,2,2-tetrachloroethane (Fluka), 1,2-dichloroethane (Merck) were reagent grade and used as-received. Nafion 117 (DuPont) was used as a reference material. Nafion 117 membranes were boiled in 1 M HCl under reflux conditions for 1–2 h and then thoroughly washed with deionized water in order to ensure complete removal of acid. The samples were then air dried and stored in sealed bottles at ambient temperature.

2.2. Grafting copolymerization process

Rectangular pieces (3 cm × 2 cm) of pristine porous films were washed with acetone and then dried in a vacuum oven (10 mbar) at 60 °C until constant weight was obtained. The monomer impregnation polymerization by means of radiation induced grafting method was used to prepare the pore-filled electrolyte membrane. Styrene is polymerized into the pores of pristine films by using simultaneous irradiation method. Prior to the grafting reaction, the films were saturated with known volume of monomer solution diluted with solvent, i.e. toluene for 24 h in glass ampoules. The excess monomer solution was removed by wiping the film surfaces with tissue papers. The irradiation experiments were carried out using an electron beam accelerator (EPS3000, NHV Nissan) under the conditions shown in Table 1. All samples were irradiated several times in order to reach the total dose by cycling the process. The total overall irradiation times for all samples are dependent on the total dose required.

After grafting, the films were subsequently rinsed overnight in toluene at room temperature and ultrasonically extracted in order to remove the residual monomer and homopolymer adhering to the polystyrene pore-filled film's surfaces and then dried in a vacuum oven at 60 °C and 1.333224 × 10^2 Pa [1 Torr]. The extraction process was re-

Table 1
Conditions at which irradiation were carried out by electron beam accelerator

Accelerating voltage (MeV)	0.5
Beam current (mA)	1.0
Distance from window (cm)	20
Irradiation length (m)	2.3
Conveyor speed (m/min)	2.9
Dose per pass (kGy)	5
Dose range (kGy)	5–25
Duration (min)	0.8–4.0 (48–238 s)
Atmosphere	N$_2$
Temperature	Ambient

peated a few times until a constant weight was obtained. The grafting yield of styrene anchored in the pore-filled films was expressed in the following equation:

$$\text{Grafting yield, } Y \, (\%) = \frac{W_g - W_o}{W_o} \times 100 \tag{2.1}$$

where W_g and W_o are the weights of polystyrene pore-filled and original films, respectively.

2.3. Sulfonation process

Polystyrene pore-filled films were initially washed with dichloromethane, soaked therein for 30 min, and then removed and dried in a vacuum oven for 1 h. The pore-filled films were then sulfonated by using a sulfonation mixture composed of 20 vol.% chlorosulfonic acid and 80 vol.% 1,1,2,2-tetrachloroethane. The sulfonation was performed in a glass reactor containing both the pore-filled films and the sulfonation mixture, while the temperature of the reactor was maintained at approximately 80 ± 10 °C by means of an oil bath. The sulfonation reaction was allowed to continue for 12 h under N$_2$ atmosphere.

Sulfonated polystyrene pore-filled electrolyte membranes were then removed and thoroughly rinsed with 1,1,2,2-tetrachloroethane, dichloromethane and tetrahydrofuran in order to remove the excess of chlorosulfonic acid. These resulting 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 thoroughly washed with deionized water in order to ensure complete removal of acid, and finally stored in sealed bottles at ambient temperature.

2.4. Swelling behavior

The swelling behaviors of the resulting membranes were studied as a function of water and methanol uptakes, respectively. The dry weight of the samples was initially measured after drying in vacuum oven (16 h, 80 °C and 1.333224 × 10^{-1} Pa [10^{-3} Torr]) and then over silica gel in an evacuated desiccator's for 1 h. The samples (3 cm × 2 cm) were immersed in water or in methanol, which placed in a glass container at room temperature for about 1 day. After complete immersion, the swollen samples were removed and

the excess of water adhering to the surface was quickly wiped with absorbent paper and weighed immediately in a closed balance.

The water uptake is defined as the percentage of the weight increase in the dry membrane using the following equation:

$$WU = \frac{w_{wet} - w_{dry}}{w_{dry}} \qquad (2.2)$$

where w_{dry} is the mass of the dried sample and w_{wet} the mass of the wet sample, respectively.

The hydration number, i.e. the number of water or methanol molecules per sulfonic acid groups was calculated on the basis of the water uptake by weight and concentration of sulfonic acid group. Thus, this hydration number is defined as

$$\text{Hydration number} = \frac{w_x\{M_{styrene}(1 + GY/100) \\ + ((GY/100)(SY/100))M_{SO_3H}\}}{M_x[(GY/100)(SY/100)]w_{dry}} \qquad (2.3)$$

where w_x is the mass of absorbed water, w_{dry} the mass of dry membrane, $M_{styrene}$ the molecular weight of styrene, M_{SO_3H} the molecular weight of sulfonic acid group, M_x the molecular weight of H_2O or CH_3OH, GY the grafting yield and SY the sulfonation yield.

2.5. Ion exchange capacity (IEC)

The ion exchange capacity (meq/g) of the membranes were determined by acid–base titration technique. The dried membrane samples (3 cm × 2 cm) in acid form were equilibrated in 50 ml of 0.5 M KCl overnight at room temperature with frequent stirring. The amount of proton (H^+) released in the solution was then titrated to a cresol red endpoint with 0.05 M KOH. After titration, the membrane samples were converted into acid form again by boiling with 3.5 M HCl for 3 h and washed free of acid. The membrane samples were then dried in vacuum oven (1.333224×10^2 Pa [1 Torr], 60 °C) overnight. The dry weight of the membranes was determined after keeping it in a desiccator at ambient temperature over fresh silica gel for 30 min. The ion exchange capacity (IEC) of the dry membrane per unit mass (meq/g) was calculated from the following relationship:

$$IEC_{experimental} = \frac{V_{KOH} \times 0.05}{m_{dry}} \qquad (2.4)$$

where V_{KOH} is the volume of KOH consumed and m_{dry} the mass of the dried sample.

The degree of sulfonation was defined as an ion exchange capacity (IEC) equivalent to one $-SO_3H$ group per aromatic ring as reported by Walsby et al. [7]:

$$\text{Sulfonation yield (\%)} = \frac{IEC_{experimental} \times 100}{IEC_{theory}} \qquad (2.5)$$

where IEC_{theory} is the ion exchange capacity calculated from the grafting yield which was given by the following equation [7]:

$$IEC_{theory} = \frac{9.62Y}{100 + 1.77Y} \qquad (2.6)$$

where Y is the grafting yield of the pore-filled film.

The equivalent weight (EW) was calculated from the following equation, which is reported as [8]

$$EW = \frac{1000}{IEC} \qquad (2.7)$$

2.6. Conductivity

Prior to conductivity measurements, the membranes were first transformed into protonic or acidic form. The proton conductivity of the membrane was measured with a LCR meter (Agilent HP 4284A) by using a frequency range of 20 Hz–1 MHz. The impedance studies were conducted using temperature ranges from ambient to 80 °C. The resistance (R) was obtained from the intercept of the impedance curve with real axis at high frequency end. The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma\,(\Omega^{-1}\,cm^{-1}) = \frac{L}{RA} \qquad (2.8)$$

where L is the thickness of the membrane sample, A or (πr^2) the sample surface area and R the resistance.

3. Results and discussion

3.1. Irradiation dose

The simultaneous grafting of styrene into porous PTFE film was studied in order to determine the optimum conditions for the preparation of membrane with desired grafting yield. Fig. 1 illustrates the pore-filling ratio of styrene anchored into the PTFE films as a function of irradiation dose for different monomer concentration. The effect of the
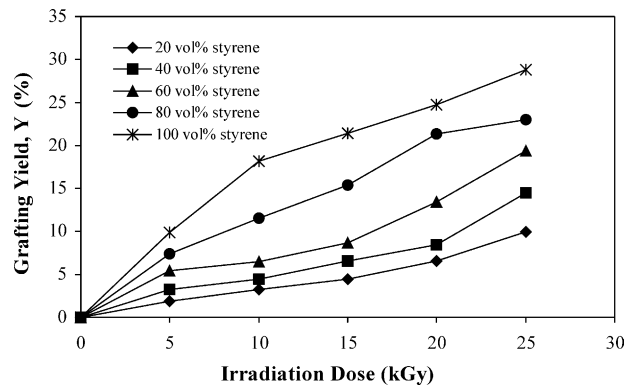

Fig. 1. Variation of the grafting yield of polystyrene pore-filled PTFE films with various monomer concentrations as a function of irradiation dose.
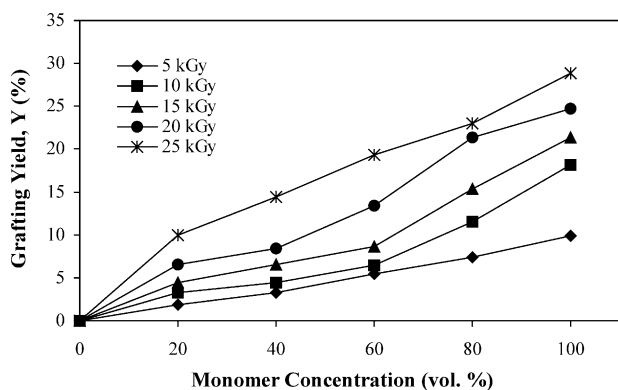
Fig. 2. Variation of the grafting yield of polystyrene pore-filled PTFE films with various irradiation doses as a function of monomer concentration.

irradiation dose on the grafting yield was studied in the range of 5–25 kGy at constant 5 kGy per pass. As shown in Fig. 1, the grafting yield increases gradually with the increased in the irradiation dose. This can be explained based on the fact that with the increasing of the irradiation dose, the production rate of radicals formation within the grafting system was also rising up. Therefore, more radicals are available to take part in the monomer impregnation copolymerization reaction that consequently increases the grafting yield of the resulting film. These results coincide with the result of previous researchers, who found that the grafting yield could be controlled by varying the irradiation dose [5,9–11].

3.2. Monomer concentration

Fig. 2 illustrates the grafting yield for various irradiation dose of styrene grafting into the porous PTFE film

as a function of monomer concentration ranging from 20 to 100 vol.%. This volume percentage corresponds to the amount of monomer absorbed into the pores and retained on the surfaces of the pristine film. As shown in Fig. 2, the extend of grafting yield only moderately increases with monomer concentration over most of the range studied, but relatively an abrupt increase in grafting yield values are observed in the bulk monomer concentration, which suggests better monomer diffusivity into the film pores in the absence of solvent. The amount of grafting yield anchored in the pore-filled films are governed by the monomer diffusivity through the film, its concentration in the grafting layers and also the effect of irradiation dose that correlates to the amount of radical formed within the polymer matrix.

The acceleration of the grafting yield in 100 vol.% monomer concentration is assumed to be due to the increase in the availability of the monomer to the radical sites and also the capability of the polymer backbone radical to capture the styrene radical that depends on the monomer concentration presence in its vicinity. Furthermore, higher irradiation dose results in the enhancement of the anchored polystyrene grafts into the interior of PTFE film. This finding is relatively in agreement with the results of Zhi-Li et al. [12], who studied the radiation graft copolymerization of vinylimidazole (VI) onto PTFE films, respectively.

3.3. FTIR spectroscopy

Fig. 3 represents the FTIR-ATR spectra of pristine PTFE film, polystyrene pore-filled PTFE film (Y: 24.59%) and sulfonated polystyrene pore-filled electrolyte PTFE membrane (Y: 24.59%), respectively. The pristine PTFE film consists of a backbone made up of CF_2 groups. Strong transmittance due to stretching vibration of the CF_2 groups presented in the pris-
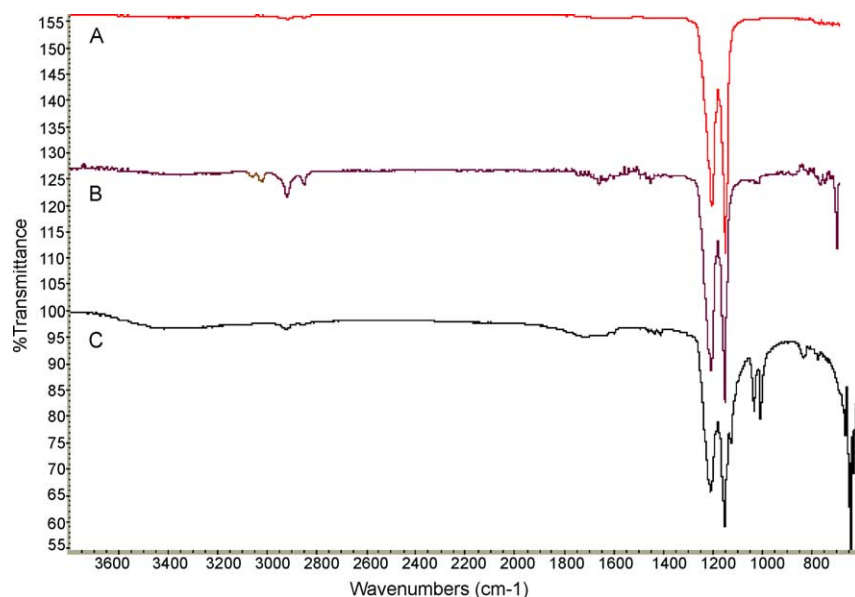

Fig. 3. FTIR-ATR spectra of: (A) pristine porous PTFE, (B) polystyrene pore-filled PTFE film (Y: 24.59%) and (C) sulfonated polystyrene pore-filled electrolyte PTFE membrane (Y: 24.59%).

tine PTFE film was found at bands of 1140–1210 cm^{-1}. The successful introduction of the benzene rings of polystyrene grafts is confirmed by the =C−H stretching vibration at 3020–3050 cm^{-1} and the skeletal C=C in plane and stretching vibration at 1500 and 1650 cm^{-1}, respectively. The aromatic C−H deformation band in the region 600–850 cm^{-1}, the C−H bending overtone and the combination band patterns within the region 1650–1800 cm^{-1} confirms the mono substitution of the benzene rings. The symmetric and asymmetric stretching of aliphatic CH$_2$ groups is attributed to the bands at 2840–2900 and 2900–3000 cm^{-1}, respectively. These features proved that styrene was filled into the PTFE film.

After sulfonation, the emergence of three new peaks was observed approximately at 1002, 1035 and 1121 cm^{-1}, respectively, confirming that the pore-filled film was sulfonated by the introduction of SO$_3^-$ groups as shown in Fig. 3 (spectra C). The broad band at 3400 cm^{-1} is attributed to the presence of −OH of water molecules associated with SO$_3^-$ groups. The relative ratio of the peak area at 1035 and 1650 cm^{-1} which represented the existence of SO$_3^-$ and polystyrene, respectively, reflected to a degree of sulfonation close to 100% achieved. It is vital to mention that similar spectra for sulfonated polystyrene pore-filled electrolyte PTFE membrane could not be produced compared to the polystyrene pore-filled PTFE film. This is due to the interference resulted from the water associated with the sulfonic groups available in the sulfonated polystyrene pore-filled electrolyte membranes. These results are in good agreement with those reported by Nasef et al. [10,13,14] and Sato et al. [15] for styrene grafted and sulfonated PTFE membrane.

3.4. Swelling behavior

Swelling behavior is regarded as one of the important characteristic properties for the sulfonated pore-filled polystyrene electrolyte membranes, which confirmed the successful incorporation of hydrophilic group inside the membrane. The water and methanol uptakes capabilities that in turn related to the membranes electrochemical properties was also determined. In this study, the swelling behavior for sulfonated polystyrene pore-filled electrolyte PTFE membranes consist of grafting yield in the range of 5.45–28.85% was investigated in terms of solvent uptake (water and methanol) and hydration number, i.e. the number of water or methanol molecules per sulfonic acid group (H$_2$O/SO$_3$H or CH$_3$OH/SO$_3$H ratios).

The percentage of the solvent uptake (i.e. water and methanol) with various grafting yield is plotted in Fig. 4. It can be seen that the sorption of both solvents by sulfonated polystyrene pore-filled electrolyte PTFE membrane increases with the increase in grafting yield. The solvent uptake increase from 7.28 to 32.07 and 3.15 to 16.75 wt.% as the grafting yield increases from 5.45 to 28.85% for water and methanol, respectively. The increase in both solvent uptakes for all membranes samples can be reasonably attributed to the increase in the hydrophilicity imparted to the membranes
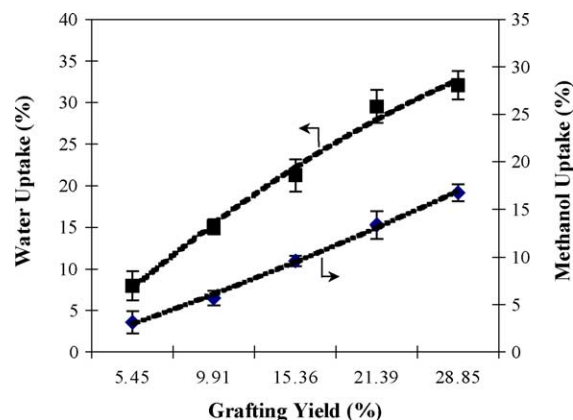

Fig. 4. Water and methanol uptakes for sulfonated polystyrene pore-filled electrolyte PTFE membranes as a function of the grafting yield.

by the incorporation of sulfonic acid groups as consequences from the increases in the grafting yield. The experiential water uptake values are found to be lower than the bulk polymer gel (namely as bulk polystyrene sulfonic acid) that is approximately 90 wt.% water uptakes as reported by Yamaguchi et al. [5] and Nasef et al. [10]. Such behavior is due to the effect of the suppression of the swelling by the porous hydrophobic PTFE matrix structure. The water uptakes of Nafion 117 membrane were found to be about 20 wt.% under the same condition conducted.

However, the water uptake values for these sulfonated membranes were observed to be higher than methanol uptake values. This is due to the degree of swelling of polymeric membrane in solvent is proportional to the hydrogen bonding capability of the solvent. The hydrogen bonding in methanol is not as strong as it is in water. This can be understood based on the fact that the O atom does not have as much partial negative charge in methanol as it does in water because the C atom draws away some of the negative charge. Therefore, the hydrogen atom in methanol does not have as much positive charge as in water. Hence, it may be concluded that the existent of extensive swelling in water is caused by high formation of hydrogen bonding formed which enhanced the facilitation of the water absorption into the membrane.

The variation of the hydration number in water and methanol with the grafting yield is shown in Fig. 5. The hydration number is defined as the number of solvent molecules per sulfonic acid group (i.e. H$_2$O/SO$_3$H or CH$_3$OH/SO$_3$H ratios). It is observed that the hydration number is approximately 10 H$_2$O/SO$_3$H when the samples are equilibrated in water, and approximately 3 CH$_3$OH/SO$_3$H when equilibrated in methanol. Thus, the hydration number for both solvents is found to be almost independent of the grafting yield. These results can be explained based on the fact that the mobility of the sulfonated polystyrene grafts incorporated in the PTFE matrix are relatively sufficient in order to allow water penetrates easily throughout the membranes [16].
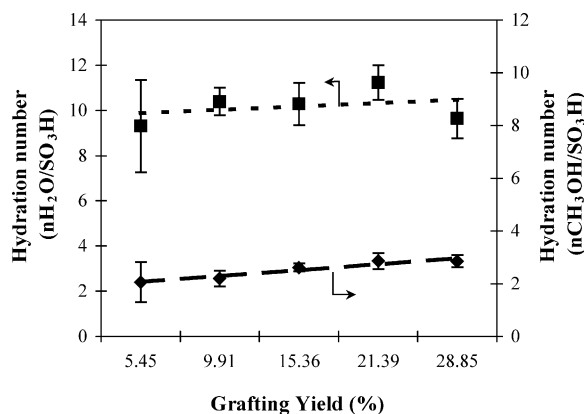
Fig. 5. Variation of the hydration number in water and methanol for sulfonated polystyrene pore-filled electrolyte PTFE membranes as a function of the grafting yield.
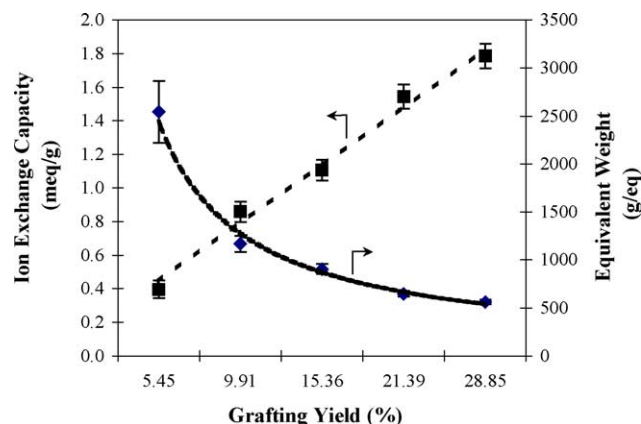

Fig. 6. The relationship between ion exchange capacity (meq/g) as well as equivalent weight (g/eq) and grafting yield of sulfonated polystyrene pore-filled electrolyte PTFE membranes.

3.5. Ion exchange capacity (IEC)

Sulfonated polystyrene pore-filled electrolyte PTFE membranes of different equivalent weights are produced through the sulfonation reactions of the pore-filled PTFE films that have various grafting yields. The sulfonation yield was determined as the ratio of sulfonic acid groups per phenyl ring groups of polystyrene anchored in the pore-filled film. The sulfonation yield and the equivalent weight for each membrane are summarized in Table 2. It can be deduced that the sulfonation yield for all membranes are approximately close to 100% which indicated that the ratio of sulfonated phenyl ring groups of polystyrene is ∼1. As can be seen from Table 1, both parameters decreases as the grafting yield is increased. This may be explained on the fact that the amount of sulfonic acid groups incorporated to the sulfonated membrane is a function of the amount of polystyrene anchored in the pore-filled film. Furthermore, these results suggest that membranes with desirable equivalent weights can be produced by controlling the grafting yield [8].

Fig. 6 shows the extent of ion exchange capacity (IEC) and equivalent weight (EW) which expressed as the milliequivalent per gram (meq/g) and gram per equivalent (g/eq) as a function of grafting yield, respectively. The IEC is observed to increase with the grafting yield in the range of 0.4–1.79 meq/g and 5.45–28.9%. The corresponding IEC value of Nafion 117 membrane is equal to 0.93 meq/g. These behaviors can be ascribed to the increase in polystyrene grafts

content within the PTFE matrix that impart more benzene ring in order to host sulfonic acids groups. Moreover, it is assumed that the sulfonated polystyrene grafts were anchored within the membrane's pores in the form of gel type electrolyte, which provides interconnected hydrophilic cationic regions through the resulting membranes [10].

According to Büchi et al. [17], the possibility of preparing membranes with tailored equivalent weight (EW) can be achieved through the implementation of radiation induced grafting method. This is due to the fact that the variation in the EW can be obtained via varying the grafting yield, which in turn, reflected on the amount of polystyrene anchored into the PTFE matrix that led to the determination of the number of sulfonic acid sites incorporated within the resulting membranes. A high grafting yield will result in a low EW of the membrane, while low grafting yield leads to high EW. Thus, the acquired EW values are in harmony with the aforementioned discussion that shows a decreasing trend with increasing grafting yield. Meanwhile, the corresponding EW value of Nafion 117 membrane is approximately to 1073 g/eq.

3.6. Proton conductivity

The proton conductivity of sulfonated polystyrene pore-filled electrolyte PTFE membranes with various grafting yields measured at room temperature is illustrated in Fig. 7. As can be seen in Fig. 7, the proton conductivity is increased with increasing grafting yield. The conductivity increases from 0.22×10^{-3} to 8.84×10^{-3} S cm^{-1} as the grafting yield increases from 5.45 to 28.85%. This is because of the ionic conductivity is a function of IEC, solvent uptake and hydration number of the membranes was found to be strongly dependence upon the grafting yield. As the grafting yield increases, more and more sulfonic acid groups are incorporated within the membranes, which led the membranes become more hydrophilic and enable to absorb more water in order to enhance the facilitation of the proton (H$^+$) mobility through the membranes. The respective conductivity value for Nafion

Table 2
Variation of the sulfonation yield and equivalent weight of sulfonated polystyrene pore-filled electrolyte PTFE membranes with various grafting yields

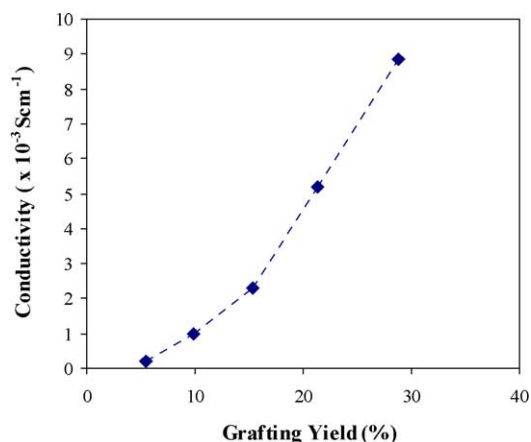| Grafting yield (%)	Sulfonation yield (%)	Equivalent weight (%)
5.45	99.71	2544
9.91	99.35	1168
15.36	98.80	905
21.39	97.81	648
28.85	96.55	560

Fig. 7. The relationship between conductivity and the grafting yield of sulfonated polystyrene pore-filled electrolyte PTFE membranes at ambient temperature.

117 is found to be approximately 1.96×10^{-3} S cm^{-1}. The decrease in Nafion's conductivity is probably due to the incomplete regeneration into acidic form during the sample preparation.

Fig. 8 displays the Arrhenius plot of the conductivity as a function of temperature for the sulfonated polystyrene pore-filled electrolyte PTFE membrane having a grafting yield of 15.36%. It is observed that there is a reasonably good correlation between the operating temperature and conductivity of the membrane. The conductivity values exhibited an increasing trend as the operating temperature increases from 303 to 353 K. As the ionic conductivity of electrolytes is thermally stimulated, it is natural to expect a rise in proton conductivity with temperature. This is due to the fact that temperature plays an essential role in overcoming activation barriers for proton mobility [18]. Within this temperature range, variation in moisture content is less significant than temperature increase in overcoming the transport activation energy barrier. In addition, the activation energy E_a
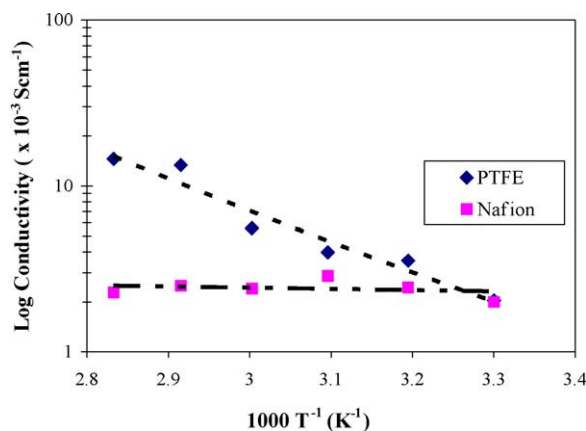

Fig. 8. Proton conductivity–temperature dependence of sulfonated polystyrene pore-filled electrolyte PTFE membrane having a grafting yield of 15.36%.

according to the Arrhenius equation $[\sigma = \sigma_0 \exp(-E_a/RT)]$ is approximately 24 and 0.411 kJ mol^{-1} for the sulfonated polystyrene pore-filled electrolyte PTFE membrane and Nafion 117, respectively. Since the activation energy of conduction is an indication of the proton mobility, it is apparent that the influence of operating temperature upon the ionic mobility of the membrane is still exists, even though formerly the membrane is saturated with water. Higher activation energy value indicates the reduction in proton mobility within the membrane and vice versa [19].

4. Conclusions

Sulfonated polystyrene pore-filled electrolyte membranes have been successfully prepared via simultaneous radiation induced graft copolymerization and subsequent sulfonation after saturating the films' pores with styrene monomer. From the research conducted and the preceding discussion, there are several conclusions have been drawn:

1. Grafting conditions were found to have pronounced effects on the grafting yield of the polystyrene pore-filled films. The grafting yields of these films were found to increase with the irradiation dose and monomer (i.e. styrene) concentration. The radiation dose in the range of 15–30 kGy and the bulk monomer concentration were observed to provide sufficient grafting yield and formed relatively homogeneous distribution of the grafts presented through the polystyrene pore-filled films. Hence, by employing such proper combinations of the irradiation dose and monomer concentration, the resulting membranes with desired properties can be acquired.

2. The solvent uptake for the sulfonated polystyrene pore-filled electrolyte PTFE membranes shows an increasing trend with the grafting yield. The water uptake values and the hydration number (H$_2$O/SO$_3$H) for PTFE matrix are approximately twice as compared with the methanol uptake values. This behavior can be ascribed to the fact that the degree of swelling of polymeric membrane in solvent is proportional to the hydrogen bonding capability of the solvent.

3. The IEC and EW of the sulfonated polystyrene pore-filled electrolyte PTFE membranes depend mainly on the grafting yield. It is obvious that the IEC increases in contrast to the EW that decreases as the grafting yield increases, respectively. Such behaviors is evident due to the fact that with increasing grafting yield, progressively more sulfonic acid groups are incorporated within the resulting membrane.

4. Based on the aforementioned discussion, it can be concluded that the proton conductivity for the resulting membranes is a function of both moisture content and temperature. The measured conductivity of the sulfonated polystyrene pore-filled electrolyte PTFE membranes was approximately within the magnitude of 10^{-3}

and 10^{-2} S cm^{-1} at room temperature and at higher operating temperature, respectively.

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