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Radiation-induced grafting of styrene onto ultra-high molecular weight polyethylene powder for polymer electrolyte fuel cell application II. Sulfonation and characterization[%]

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ABSTRACT

Post-sulfonation of selective styrene-grafted ultra-high molecular weight polyethylene (UHMWPE-g-PS) films was carried out by chlorosulfonic acid and the properties of the membranes were investigated. The UHMWPE-g-PS films were previously prepared by initial γ -irradiation of polyethylene powder, grafting with styrene, followed by hot-pressing to process into films. The range of ion exchange capacities (*IECS*) obtained with different degrees of grafting (*DG*) of styrene was in the range of 0.97–2.77 mequiv./g. The water and methanol uptake of sulfonated films were studied on a weight and volume basis. FTIR spectroscopy and thermal gravimetric analysis (TGA) of control UHMWPE, UHMWPE-g-PS, and UHMWPE-g-PSSA were compared. The methanol permeability values at 30 °C for the series of UHMWPE-g-PSSA membranes were in the range 4.86 × 10⁻⁸ to 1.67 × 10⁻⁶ cm²/s, with corresponding proton conductivities of 0.025–0.29 S/cm at 90 °C. The methanol permeability values of UHMWPE-g-PSSA were generally lower than that of Nafion 117 for comparable or even higher proton conductivity. Transmission electron microscopy (TEM) analysis was used to observe microstructure for evidence of nanophase separation of hydrophibic and hydrophobic domains. Owing to its low cost and the results of the current study, UHMWPE-g-PSSA is suggested as a viable proton exchange membrane for low temperature hydrogen and direct methanol fuel cell applications.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications [1,2]. Proton conductive polyelectrolyte membranes (PEMs) are one of the key components in PEMFCs, which function to separate the reactant gases and conduct protons from the anode to the cathode [3]. Commercial PEMs are based mainly on perfluorinated sulfonic acid (PFSA) membrane materials, such as Nafion[®] (Du Pont, USA), Flemion[®] (Asahi Glass, Japan) and Aciplex[®] (Asahi Kasei, Japan). However, one of the key issues of PFSA-based PEMs is that dehydration occurs when used at temperatures above 80 °C, leading to lower proton conductivity [4]. In addition, the performance of PFSA-based direct-methanol fuel cells (DMFCs) is affected negatively due to the high permeability of methanol through the membrane, also known as methanol crossover [5]. Moreover, complex fluorine chemistry and raw material price of PFSA membranes contributes to their continuing high cost. The current price for Nafion membranes is of the order of US \$100 per kilowatt of generated electric power [6]. These factors, in addition to environmental recycling uncertainties of perfluorinated membranes, have combined to limit their widespread commercial application in PEMFC and DMFC [7,8]. Currently, there is much ongoing research for developing non-perfluorinated polymers with better performance and lower cost as alternative PEM materials [7,9–11].

Besides the development of new polymer, the synthesis of PEM materials through grafting of functional monomer onto commodity polymer, followed by sulfonation is an attractive option [12]. Ionizing radiation such as γ -rays and electron beams are preferably used for radiation grafting reactions due to the facts that (1) there is relatively uniform formation of radicals with a thickness of the order of mm, (2) the process is free from contamination because it does not need initiator for radical formation, so that the purity of the processed products may be maintained [13].

Almost all commercially available fluorinated polymers, such as polytetrafluoroethylene (PTFE) [14,15], Teflon-FEP [16,17],

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fluorinated ethylene propylene copolymer (FEP) [18,19], tetrafluoroethylene perfluoro(propyl vinyl ether) copolymer (PFA) [20,21], poly(vinylidene fluoride) (PVDF) [22,23], ethylenetetrafluoroethylene copolymer (ETFE) [24,25], polychlorotrifluoroethylene (PCTFE) [26], etc., have been reported as being used for radiation-induced grafting with styrene using either simultaneous irradiation or pre-irradiation methods. Irradiation of polymer with ionization radiation produces several other chemical effects such as degradation, crosslinking, and co-polymerization, along with the desired grafting reaction in the presence of monomer [27]. Therefore, in the context of radiation grafting, the main disadvantage associated with fluorinated polymers in general is that they undergo main chain scission due to the relatively stronger C-F bond as compared with the C-C bond; thus a relatively low irradiation dose can effectively reduce the molecular weight of the PTFE [28-29]. Consequently, fluorinated polymers may not be the optimal substrates for radiation-induced grafting at low temperature. However, they could be crosslinked by irradiation above the melting temperature under an oxygen-free atmosphere [30]. In the present work, non-fluorinated polymer with grafting capability is being investigated as an alternative option for PEM development through the radiation grafting technique.

Ultra-high molecular weight polyethylene (UHMWPE) has long linear chains and high crystallinity, which provide chemical inertness and good mechanical strength [31]. Owing to its excellent bulk physical and chemical properties and low cost in comparison with perfluorinated polymer, UHMWPE appears to be a promising base material for the development of alternative hydrocarbon-based PEMs, after modification.

The grafting conditions and grafting reaction kinetics of styrene onto UHMWPE powder and the subsequent film formation process have already been discussed in our previous article [32]. The present work reports on the chlorosulfonic acid post-sulfonation reaction of various films of pre-irradiation styrene-grafted UHMWPE having different levels of grafting. The term post-sulfonation is used here to distinguish pre-fabricated films that were sulfonated, rather than films fabricated from sulfonated styrene-grafted polymer. Chlorosulfonic acid introduces sulfonic acid groups onto the styrene residue of grafted films, ultimately providing inexpensive PEM materials. This work is possibly one of the first detailed studies of PEM materials based on the post-sulfonation of films prepared by radiation-induced grafting of styrene onto UHMWPE. The study includes measurements of ion exchange capacity (IEC), degree of substitution (DS), water and methanol uptake. Membranes were also characterized by attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR), thermal gravimetric analysis (TGA) and transmission electron microscopy (TEM). Measurements of proton conductivities and methanol permeabilities are also included.

2. Characterization and measurements

2.1. Materials

Styrene-grafted UHMWPE (UHMWPE-g-PS) films with a thickness of $80 \pm 5 \,\mu$ m having different degree of grafting (*DG*) were prepared in our previous study. Styrene was first grafted onto UHMWPE and subsequently hot-pressed into film; the details of the grafting reaction and film formation were described [32]. The polymer sample size was 2 g for each of the grafting reactions. Chlorosulfonic acid (CISO₃H) and 1,2-dichloroethane were obtained from Sigma–Aldrich Chemical Corp. Analytical grade dichloromethane was obtained from EMD Ltd. All chemicals were used as received.

2.2. Measurements

Following the styrene grafting reactions, the polymers were washed and dried under vacuum until constant weight was reached. The degree of grafting was obtained by using the following equation:

degree of grafting(%) =
$$\frac{W_g - W_0}{W_0} \times 100$$
 (1)

where W_0 and W_g are the weights of polymer before and after the grafting reaction, respectively.

Sulfonation of the UHMWPE-g-PS films was carried out by immersing the films in a 0.2 M chlorosulfonic acid solution in dichloroethane for an initial period of 5 h at 50 °C, followed by overnight immersion at room temperature. After sulfonation, the membranes were removed from the sulfonating solution and immersed in fresh dichloromethane for 3 h, followed by washing with dichloromethane, the films were thoroughly washed with deionized water.

2.3. Ion exchange capacity and degree of substitution

IEC of the sulfonated polymers was measured using a typical titration method. The dried membrane in the protonic form was immersed into 25.00 mL of 3 M NaCl solution for 24 h. A large excess of Na⁺ ions in the solution ensured nearly complete ion exchange. Then, 10.00 mL of the 3 M NaCl solution containing the released H⁺ ions was titrated against 0.05 M NaOH solution using phenolph-thalein as indicator. The *IEC* was calculated using the following equation:

$$IEC_{exp} = \frac{0.05 \times V_{NaOH} \times n}{W_{dry}} \text{ (mequiv./g)}$$
(2)

where V_{NaOH} (mL) is the volume of the 0.05 M NaOH solution used for titration. *n* is the factor corresponding to the ratio of the amount of NaCl solution taken to immerse the polymer (25.00 mL) to the amount used for titration (10.00 mL), which is 2.5. W_{dry} (g) is the dry weight of the polymer electrolyte membrane in the protonic form.

Theoretical $IEC(IEC_{theory})$ can be calculated, making the assumption that 100% sulfonation of the grafted styrene occurs, i.e., one sulfonic acid group per styrene unit, by applying the following equation [33]:

$$IEC_{\text{theory}} = \frac{1000 \times DG/M_{\text{styrene}}}{100 + DG + (DG/M_{\text{styrene}}) \times M_{\text{sulfonate}}} \quad (\text{mequiv./g}) \quad (3)$$

where M_{styrene} is the molar weight of styrene unit and $M_{\text{sulfonate}}$ is the additional molar weight due to sulfonate.

The *DS* of sulfonic acid group indicates the percentage sulfonation level of the grafted styrene and can be calculated by simple relationship between experimental and theoretical *IEC* values as represented in the following equation:

$$DS = \frac{IEC_{exp}}{IEC_{theory}} \times 100$$
(4)

2.4. Water and methanol uptake

The water uptake and methanol uptake of the previously vacuum dried membranes in the sulfonic acid form were measured for 30 h in deionized water and methanol, respectively. The reported measurements are based on the average of two readings of each sample of dimension about $30 \text{ mm} \times 30 \text{ mm}$. Water uptake was measured at 30 and 80 °C while methanol uptake was measured at 30 °C. The temperature was controlled by means of a thermostatic

water bath. Before measuring weights and volume of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel. The same procedure was used to measure methanol uptake. The weight percentage uptake of water and methanol can be determined by using the following equation:

weight uptake (%) =
$$\frac{W_w - W_d}{W_d} \times 100$$
 (5)

where W_w is the weight of the swollen membrane and W_d is the weight of the dried membrane. Similarly the volume percentage uptake of water and methanol can be evaluated using the following equation:

volume uptake(%) =
$$\frac{V_w - V_d}{V_d} \times 100$$
 (6)

where V_w is the volume of the swollen membrane V_d is the volume of the dried membrane. A thickness gauge with a resolution of 0.005 mm was used to measure the membrane thickness. The length and width of the membrane samples were determined by using a digital sliding calliper with a resolution of 0.01 mm.

2.5. Membrane characterization

The FTIR-ATR analyses were performed on a Varian FTIR 1000 (Schimitar Series) using control, styrene-grafted, and sulfonated styrene-grafted UHMWPE films. The thermal stability of the membranes was investigated by thermogravimetric analysis using a TA Instruments thermogravimetric analyzer (TGA) instrument model 2950. Polymer samples (~14 mg each) for TGA analysis were preheated at 100 °C for 40 min under nitrogen atmosphere to remove moisture. Samples were then heated at 10 °C/min from 50 to 700 °C under nitrogen atmosphere.

2.6. Proton conductivity

Proton conductivity measurements were of the UHMWPE-g-PSSA membranes were derived from AC impedance spectroscopy measurements over a frequency range of 1 to 10^7 Hz with an oscillating voltage of 50-500 mV, using a system based on a Solatron 1260 gain phase analyzer. Each membrane sample was cut into sections 2.5 cm \times 1 cm prior to being mounted in the cell. The cell was placed in a temperature controlled container open to air by a pinhole where the sample was equilibrated at 100% RH at ambient atmospheric pressure and clamped between two electrodes. The proton conductivities of the samples were measured in the longitudinal direction and were calculated from the impedance data, using the following relationship:

$$\sigma = \frac{l}{RS} \tag{7}$$

where σ is the proton conductivity (in S/cm), l is the distance between the electrodes used to measure the potential (l=1 cm), S is the membrane cross-sectional surface area (membrane width × membrane thickness) for protons to transport through the membrane (in cm²) and R is derived from the low intersection of the high frequency semicircle on a complex impedance plane with the Re (Z) axis.

2.7. Methanol permeability

The permeability experiments were carried out utilizing a glass diffusion cell. One compartment of the cell ($V_A = 100 \text{ mL}$) was filled with a solution of methanol (10 vol.%) and 1-butanol (0.2 vol.%) in deionized water. The other ($V_B = 100 \text{ mL}$) was filled with 1-butanol

(0.2 vol.%) solution in deionized water. The membrane was clamped between the two compartments and both of these were stirred throughout the experiment. A flux of methanol sets up across the membrane as a result of the concentration difference between the two compartments. A detailed description of the experimental set-up and procedure can be found elsewhere [34]. The methanol concentration in the receiving compartment as a function of time is given by the following equation:

$$C_{\rm B}(t) = \frac{A}{V_{\rm B}} \frac{DK}{L} C_{\rm A}(t-t_{\rm o}) \tag{8}$$

where C_B and C_A are the two methanol concentrations; A and L are the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution. Assumptions are made here that D inside the membrane is constant and K does not depend on concentration. The product $D \cdot K$ is the membrane permeability. Time lag t_0 is explicitly related to the diffusivity: $t_0 = L^2/6D$ [35]. C_B was measured at several time intervals during an experiment and the permeability was calculated from the slope of the straight line. Methanol concentrations were determined by ¹H NMR spectroscopy using solutions taken directly from the diffusion cell. without the use of deuterated solvents. Shimming was done using the ¹H resonance of H_2O . 1-Butanol in D_2O was used as the internal reference standard. During permeability tests the temperature was controlled at 30 °C by means of a thermostatic water bath.

2.8. TEM analysis

TEM samples were stained by immersing films in lead acetate aqueous solution for 24 h, thoroughly washed with water, and dried at room temperature. Lead acetate is used to exchange the sulfonic acid groups with a lead counter ion, enabling hydrophilic regions to be observed as darker areas. The polymer samples were embedded in polystyrene. Specimen microtomy was performed using Reichert-Jung UltraCut E. A sample slice was placed onto a 300 mesh carbon-coated holey TEM copper grid and was dried in vacuum. The dried grid was then loaded into a double tilt sample holder. The sample was thus examined with a Philips CM20 STEM equipped with a Gatan UltraScan 1000 CCD camera combined with Digital Micrograph Software (dm3.4) and an energy dispersive Xray spectrometer: INCA Energy TEM 200. TEM images were taken at 120 kV.

3. Results and discussion

3.1. Ion exchange capacity/degree of substitution

The DG of styrene onto pre-irradiated UHMWPE was quantified using Eq. (1). A detailed study of grafting reaction kinetics and the film formation process was already discussed elsewhere [32]. Ion exchange sites were introduced by post-sulfonation of UHMWPE-g-PS films, where sulfonic acid groups were attached to the aromatic rings of PS graft. The number of sulfonic acid groups per unit mass of polymer was determined experimentally by measuring the IEC. The theoretical IEC was also calculated on the basis of degree of grafting and making the assumption that each styrene residue unit is substituted with one sulfonic acid group. DS of sulfonic acid group to the grafted membrane is assessed by measuring the ratio of experimental IEC to the theoretical IEC. Fig. 1 shows the relationship of degree of grafting with IEC and DS. The IEC increases with the degree of grafting. There is a good agreement between experimental and theoretical values of the IEC at lower degree of grafting levels; however the deviation between the calculated and experimental values increases



Fig. 1. Variation of IEC, DS and EW of UHMWPE-g-PSSA membranes with %DG.

with the increase in degree of grafting, which may be explained by incomplete sulfonation in UHMWPE-g-PS with high degree of grafting.

In contrast with many other grafting studies, UHMWPE powder, rather than film, was used for the grafting reaction. Grafting on powder may be considered as a better experimental option for improving the penetration of styrene monomer into the amorphous sites of the polymer, where grafting has to take place [36]. The grafted powder was then fabricated into film by hot-press processing before sulfonation.

In many previous studies, a wide variation in the DS was observed when film (rather than powder in the present study) was used as substrate for the grafting reaction and subsequently sulfonated [37,38]. The origin of this variation is due to the local differences in graft level due to inhomogeneities over the area of the membrane. In the present study of powder grafting, there is more homogeneity in the grafting reaction. The observed decrease in DS at high degree of grafting is primarily due to the penetration of the sulfonating agent to the grafting site after film formation. In the literature, a wide range of degree of grafting is reported in connection with radiation-grafted membranes intended for application in fuel cells. Yet, practical degrees of grafting for membranes tested in single cells are typically between 15% and 40% [39], depending on the polymer structure. The limits are determined on the one hand by the threshold for graft penetration through the entire thickness of the film at low graft levels, below which, the membrane is not expected to have any appreciable conductivity, rendering it useless for the fuel cell. On the other hand, an upper practical limit for the graft level is given by the excessive swelling of the polymer and associated deterioration of membrane integrity, limiting the applicability and lifetime of the material. Characterization in the subsequent section provides property values to indicate optimum graft levels of UHMWPE-g-PSSA for use as a PEM.

3.2. Equivalent weight

One important parameter used to characterize ionomers is the equivalent weight. Equivalent weight (*EW*) is defined as the weight of the polymer in acid form required to neutralize one equivalent of NaOH. *EW* can be calculated using *IEC* values by using the following equation:

equivalent weight
$$(EW) = \frac{1000}{IEC(mequiv./g)}(g/equiv.)$$
 (9)

Higher *EW* values infer that there are fewer active ionic species (i.e., protons) present. Hence, PEMs with lower *EW* generally exhibit higher proton conductivities, until high dimensional swelling results. Lowering the *EW* too much is generally not practical for making useful PEMs because of the excessive amount of water (or solvent) that the polymer absorbs, resulting in partial or complete dissolution in water. Degree of grafting is an experimental parameter for controlling the *EW* of the membrane, since the *DS* is related to the *DG*. The bars in Fig. 1 show that the *EW* of the UHMWPE-g-PSSA decreased gradually with increase in the degree of grafting. A UHMWPE-g-PSSA PEM with a low *EW* value of 442 (Nafion 117 *EW* is 1100) had high proton conductivity and low methanol permeability as presented in Table 1, without excessive water uptake.

3.3. FTIR-ATR analysis

Fig. 2 represents the FTIR-ATR spectra of pristine UHMWPE, styrene-grafted UHMWPE and sulfonated styrene-grafted UHMWPE films with different degree of grafting. UHMWPEg-PS films with DG up to 44% obtained by the pre-irradiation technique were analyzed as shown by curves b-d. Evidence for substitution on polvethylene at C-H is shown by the 1472 cm⁻¹ C-H stretching and 1463 cm⁻¹ C-H bending absorption bands of the pure UHMWPE sample being suppressed as the degree of grafting increases. Medium to weak bands appeared at 1454, 1495 and 1604 cm⁻¹, which are attributed to the skeletal in-plane deformation of conjugated C=C of the benzene ring. The absorption bands in the ranges of 2825–2870 and 2870–2960 cm^{-1} are characteristic bands for symmetric and asymmetric stretching of aliphatic -CH₂ groups. These spectral features provide supporting evidence that styrene was grafted into the UHMWPE film.

The emergence of new bands in curves e–g was observed in the region between 1000 and $1200 \,\mathrm{cm}^{-1}$. The absorption band at $1035 \,\mathrm{cm}^{-1}$ is attributed to in-plane C–H bending vibration of the para-disubstituted benzene ring, and those at 1130 and 1006 cm⁻¹ are due to symmetric and asymmetric stretching vibration of S=0. These characteristic absorption bands increased with *DG* and *IEC*, thus indicating that the grafted films were sulfonated by the introduction of SO₃H groups and the amount of substituted SO₃H groups increases according to the *DG* of the membrane.

Table 1

Physico-chemical properties of UHMWPE-g-PSSA membranes compared to Nafion 117.

Sample	DG (%)	IEC (mequiv./g)	EW	Water uptake		Methanol uptake		Proton conductivity (mS/cm)			MeOH perm. (cm ² /s)
				(wt.%), 30°C	(vol.%), 30 °C	(wt.%), 30°C	(vol.%), 30°C	35°C	90°C	100°C	30°C
UHMWPE-g-PSSA-12	12	0.97	1031	14.28	10.49	12.24	10.15	16	25	13	4.86×10^{-8}
UHMWPE-g-PSSA-22	22	1.5	667	33.84	22.07	16.63	13.50	61	96.7	41	2.69×10^{-7}
UHMWPE-g-PSSA-33	33	1.94	515	57.3	47.13	31.98	19.10	111	181	157	$7.68 imes 10^{-7}$
UHMWPE-g-PSSA-44	44	2.26	442	97.51	87.66	49.20	25.67	140	227	148	1.45×10^{-6}
UHMWPE-g-PSSA-58	58	2.62	381	172.39	173.82	91.04	42.09	211	290	122	$2.80 imes10^{-6}$
Nafion 117	-	0.91	1100	17.5	29.3	60	100	54	99	111	1.65×10^{-6}



Fig. 2. Comparative FTIR-ATR spectra of control, styrene-grafted, and sulfonated styrene-grafted UHMWPE.

3.4. Water and methanol uptake

The water uptake in sulfonated polymers is related to the number of ion exchange sites in the membrane and has a profound effect on proton conductivity and mechanical properties. While higher water uptake generates more solvated proton species, which is needed for high conductivity, there is trade-off between conductivity and mechanical properties if it is excessive. The methanol uptake is also an important parameter that is related to the methanol permeability of the membrane. In general, a membrane with a high methanol uptake value also behaves as highly methanol permeable. Volume percentage swelling and weight percentage swelling of styrene-grafted and sulfonated UHMWPE membranes (UHMWPE-g-PSSA) with IEC in the range of 0.97-2.27 mequiv./g was determined as a function of IEC in methanol at 30°C and in water at 30 and 80°C, as shown in Fig. 3. The percentage uptake values increased gradually in all cases with the increase of IEC; however this increase is relatively faster for IEC higher than 1.5 mequiv./g.

Since UHMWPE is almost completely insoluble in methanol [40], it results in methanol having little or no direct effect on swelling



Fig. 3. Variation in dimensional swelling and liquid uptake of UHMWPE-g-PSSA membrane with *IEC*.

of the UHMWPE-g-PSSA. Similar to water uptake, methanol uptake values are also attributed to the sulfonated part of the membrane and increased gradually with the increase in the *IEC* of the membrane.

Swelling of sulfonated polymer membranes strongly influences the transport phenomena, including proton conduction and methanol permeability, which increases directly with the increase of swelling. A comparison between the swelling as a function of volume and weight uptake is presented in Fig. 3. For a given range of *IEC*, the volume uptake of UHMWPE-g-PSSA is found to be lower compared with the weight uptake. This trend is contrary to Nafion, for which the volume uptake is higher than weight uptake (Table 1), on account of its high relative density.

3.5. Methanol permeability

The methanol permeability is the product of the diffusion coefficient and the sorption coefficient and is used to describe the transport of permeate through membranes. The diffusion coefficient is a kinetic term which shows the effect of the surrounding environment on the molecular motion of permeate and the sorption coefficient is an equilibrium term correlating the concentration of a component in the fluid phase with its concentration in the membrane polymer phase [41].

UHMWPE-g-PSSA membranes prepared from UHMWPE-g-PS membranes with DG in the range of 12-58% were evaluated for methanol permeability. The relationship of methanol permeability with %DG and IEC is presented in Fig. 4. Methanol permeability for UHMWWPE-g-PSSA (DG = 12%) was 4.86×10^{-8} cm²/s which increased with DG and reached $2.80 \times 10^{-6} \text{ cm}^2/\text{s}$ for UHMWE-g-PSSA (DG = 58%). The measured values of methanol permeability, proton conductivity and volume expansion/equilibrium sorption are combined in Table 1. Comparing the methanol permeability and volume expansion with DG of UHMWPE-g-PSSA membranes in Table 1, the value of DG statistically agrees with the value of methanol permeability and volume expansion. When compared with Nafion 117, most of the grafted membranes exhibit lower methanol permeability than Nafion, even while having a higher volume expansion. Hence it is plausible that methanol transport is influenced mainly by the kinetic factor (diffusion) instead of the equilibrium factor (sorption) for UHMWPEW-g-PSSA membranes.



Fig. 4. Relationship of methanol permeability with %DG and IEC of membranes.

3.6. Proton conductivities

Fig. 5 shows the relationship of proton conductivity with the DG and IEC at temperatures up to 90 °C and in the fully hydrated state for the UHMWPE-g-PSSA membrane series. At a given temperature, proton conductivity of UHMWPE-g-PSSA membranes increased with DG. A higher content of styrene grafted to the main chain provides more sites for the electrophilic substitution of sulfonic acid group. Consequently, membranes with higher IEC and lower equivalent weight values exhibit increased water uptake and hydration number, which leads to higher proton conduction. Typical of Nafion and other PEM materials, the proton conductivity of UHMWPE-g-PSSA membrane is also temperature dependent and increases with temperature. Since the proton conductivity mechanism of hydrated materials is due to the transport of H_3O^+ or $H_5O_2^+$, the increase in proton conductivity with temperature could possibly be attributed to the increase in the degree of hydration of sulfonic acid groups and thermal stimulation of the resultant conducting ions.

The proton conductivities of UHMWPE-g-PSSA gradually increase with *IEC* and become comparable to that of Nafion for the membrane with an *IEC* value 1.5 mequiv./g. Conductivities exceed that of Nafion at all temperatures up to 90 °C for higher *IEC* values. However the proton conductivities of the UHMWPE-g-PSSA membranes decreased at 100 °C. This may be attributed to dehydration of the membrane as well as softening of the base polymer as the melting temperature of UHMWPE is low (~142 °C for unsulfonated



Fig. 5. Relationship between proton conductivity with DG and IEC at different temperatures.



Fig. 6. AC impedance spectra for UHMWPE-g-PSSA membrane (DG=22%, IEC=1.5 mequiv./g).

polymer). The increase in proton conductivity with increase in temperature up to 90 °C is promising and suggests that the membrane may be able to operate effectively if maintained in the hydrated state up to this temperature. PEM materials with high proton conductivity and low dimensional swelling have a good potential for fuel cell application. Proton conductivities of UHMWPE-g-PSSA are as high as 0.29 S/cm at 90 °C for the 58% grafted sample, which is much higher than the value of 0.099 S/cm of Nafion 117 at 90 °C.

Nasef et al. [37] and Gubler et al. [38] outlined in detail the problems encountered during proton conduction measurements for the grafted PEMs, in which grafting was conducted on polymer film substrates. It was described that at low DG, the polystyrene grafts are located near the surface of the film while the membrane interior remains ungrafted and subsequently exerts a high local resistance to proton conduction due to inhomogeneous distribution of ion exchange sites over the area of the membrane. Thus the conductivity data obtained from their results show considerable scatter at low and medium DGs of \leq 20%, because the ac impedance spectra obtained were of poor quality and unsuitable for the extraction of meaningful numbers. Gubler et al. also confirmed the inhomogeneous distribution of ion exchange sites over the area of the membrane by observing the patchy coloring of the membranes upon the introduction of an indicator dye. It was also described that the membranes became increasingly brittle at higher graft levels, and thus could not even be used for conductivity measurements because of fracturing. Both of these challenges (1) penetration of graft throughout the membrane and (2) brittleness for high DG films, are adequately addressed in the present study by applying a new fabrication protocol, i.e., irradiation grafting modification of the base polymer in the powder, subsequent film fabrication and post-sulfonation. This methodology improved the uniformity of grafting distribution throughout the film cross-sectional volume and is confirmed by the continuity in conductivity data. The impedance curves obtained were of better quality as shown in Fig. 6 for UHMWPE-g-PSSA having a DG of 22%.

As already discussed, temperature influences the activation energy of conductive ions and hence proton conductivity. However the plot showing slopes of conductivity in Fig. 5 shows that the activation energy is lower for the samples with low *DG* and increased with an increase in the *DG*. Fig. 7 illustrates the physical appearance of UHMWPE-g-PSSA series of membranes, which shows that a membrane with even a high *DG* of 44% and *IEC* 2.26 mequiv./g remains flexible and exhibits no fragility or brittleness. These features are attributed to the uniform distribution of the styrene



Fig. 7. Left to right: Nafion 117; UHMWPE-g-PSSA (*DG* = 12%, *IEC* = 0.967); UHMWPE-g-PSSA (*DG* = 22%, *IEC* = 1.50); UHMWPE-g-PSSA (*DG* = 33%, *IEC* = 1.94); UHMWPE-g-PSSA (*DG* = 40%, *IEC* = 2.15); UHMWPE-g-PSSA (*DG* = 44%, *IEC* = 2.26).

grafted within the bulk membrane volume due to bulk grafting followed by film formation as compared with the normally reported method of radiation grafting on films, which usually exhibit nonuniformity and lack of connectivity of proton conducting channels.

It is also described in the literature [16,37,38] that as the *DG* approaches ~20%, more grafts are distributed near the membrane interior, resulting in a diminution of the local resistance. Consequently, the proton conductivity increases and an additional increase in the *DG* does not bring about considerable increases in the conductivity because of the achievement of a possibly more homogenous distribution of the sulfonated polystyrene grafts within the membrane. This discussed effect is not verified in our experimentation, where the conductivity increases gradually with *DG* up to extent of 58% grafting in the present study. A possible explanation is that when a certain level of grafting has been reached in a radiation modified film, the penetration depth may be restricted and any further grafting would be localized near the film surface, so a further increase in *DG* would have little effect on increasing proton conduction and would also contribute to membrane brittleness.

The proton conductivity at 90 °C for UHMWPE-g-PSSA (DG = 58%) of 0.277 S/cm is considerably higher than that for Nafion 117 of 0.099 S/cm, even though it has a lower methanol permeability of 1.45×10^{-6} cm²/s compared with 1.65×10^{-6} cm²/s for Nafion. Table 1 shows that the methanol permeability for UHMWPE-g-PSSA (*DG* = 58%) membranes is 2.80×10^{-6} cm²/s which is slightly higher than that of Nafion 1.65×10^{-6} cm²/s however the proton conductivity is 0.29 S/cm, which is much higher than Nafion 117 at 90 °C. This trend of lower methanol permeability, even for membranes with higher water uptake than Nafion 117 are an unusual property of the UHMWPE-g-PSSA that make it suitable for exploring in a direct methanol fuel cell.

3.7. TGA

TGA thermogram of control UHMWPE, styrene-grafted UHMWPE (UHMWPE-g-PS) and styrene-grafted and sulfonated UHMWPE (UHMWPE-g-PSSA) are presented in Fig. 8.

The TGA curve of UHMWPE shows excellent thermal stability, having negligible weight loss up to 425 °C and exhibits a single main chain degradation step started from 425 °C and ends up with 100% weight loss at 500 °C. After grafting of styrene on UHMWPE, the films contain two different structure types; one is the aliphatic backbone of UHMWPE and the other is grafted styrene aromatic units. Fig. 8 shows that UHMWPE-g-PS behaves identically to non-grafted UHMWPE towards temperature increase up to 410 °C. Above this temperature, the onset point due to weight loss of UHMWPE-g-PS was slightly lower than the onset point of UHMWPE. This difference is likely due to the degradation of grafted-styrene units

in UHMWPE-g-PS. However, this degradation stage is merged with the degradation of the aliphatic polymer backbone, such that no two weight loss stages could be distinguished. The sharpness in the weight loss at the initial stage with the increase in DG suggests that this difference in onset is due to grafted styrene units. The total weight losses for UHMWPE and UHMWPE-g-PS were 100%. 100% weight loss, confirmed by repeat experiments, was attributed to the fact that UHMWPE and UHMWPE-g-PSSA contain only carbon and hydrogen, resulting in materials that are completely vaporizable. UHMWPE-g-PSSA membranes in the sulfonic acid form behave differently in their thermal degradation pattern. There was a gradual weight loss of UHMWPE-g-PSSA membrane in the temperature range 150-260 °C, which is due to loss of water associated with sulfonic acid groups. Decomposition of sulfonic acid groups begins around 260 °C and occurs up to 400 °C; decomposition of the grafted sites occurs above 410 °C and is followed by UHMWPE main chain degradation. In contrast with the unsulfonated polymers, the total weight loss observed in sulfonated membranes is less than 100%. The quantity of residue increases with increase in IEC (amount of substituted sulfonic acid group). This is attributed to the presence of sulfur in the residue that cannot be converted into completely evaporated product during the TGA measurement.

3.8. Microstructure of the membranes

Proton conductivity, methanol permeability and dimensional stability of the membranes are closely related to their morphology. Wide ion channels formed by hydrophilic domains are helpful to the



Fig. 8. TGA curves of control UHMWPE, styrene-grafted UHMWPE (UHMWPE-g-PS) and styrene-grafted and sulfonated UHMWPE (UHMWPE-g-PSSA).



Fig. 9. Microstructure of grafted and sulfonated UHMWPE (UHMWPE-g-PSSA) membrane (*DG* = 12%, *IEC* = 0.97 mequiv./g). Bar is equivalent to 50 nm.

movement of protons, but are possibly detrimental to mechanical properties and dimensional stability in hot water and also significantly contribute in the enhancement of methanol crossover. The microstructure of the present membranes was studied by TEM, as shown in Fig. 9.

In the image, the bright portions are attributed to the non-grafted, non-sulfonated hydrophobic regions of the UHMWPEg-PSSA membrane, while the darker portions represent the hydrophilic domain arising from the sulfonation of side chain grafted styrene. In contrast with Nafion, sharp phase separation was not observed. This may be due to the presence of narrower channels that are reasonably connected that resulted in high proton conduction and low methanol permeability, as described by Kreuer [42].

The concept of narrow channels is also supported by the fact that UHMWPE has a highly crystalline nature, where grafting may only occur with amorphous regions [36]. This enhances the graft density in the amorphous region of the polymer and subsequently enhances the density of sulfonic acid group substitution following post-sulfonation, which would contribute to the high conductivity of the UHMWPE-g-PSSA membrane. Another possible reason is that entanglement of the grafted and non-grafted portion of the UHMWPE-g-PS membrane may occur during film formation by the compression moulding technique; the detailed procedure is discussed elsewhere [32]. Thus the sulfonated part of the membrane is closely attached with the non-sulfonated portion due to the entanglement caused by the stress applied during film formation. The absence of a sharp separation between hydrophobic/hydrophilic domains, as observed in Fig. 9, is thus a possible advantage that consequently contributes to the higher flexibility of the UHMWPEg-PSSA. These features are expected to reduce the electro-osmotic drag as well as the methanol permeation, as already discussed, suggesting that the UHMWPE-g-PSSA membranes are promising candidates for DMFC application.

4. Conclusions

Polymer electrolyte membranes were prepared using the method of pre-irradiation-induced graft co-polymerization of styrene onto UHMWPE powder, which was subsequently fabricated into film by hot-pressing. The styrenic graft levels obtained ranged from 12 to 58 wt.%. The resulting styrene-grafted films were post-sulfonated to afford PEM materials having various IEC values. Grafted polymers with IEC values of 0.97-2.77 mequiv./g could be readily prepared by controlling the DG from 12% to 58%. The membranes were characterized ex situ for IEC, water uptake and conductivity. The proton conductivities show an increasing trend as a function of DG, approaching the value for Nafion 117 at a DG of 22%. This gradually increased with higher DG, reaching 0.29 S/cm at 90 °C for the highest DG value of 58%. The conductivity data show a regularly increasing trend, contrary to other grafted membranes where some degree of experimental scatter was observed [38]. The regularly increasing trend is explained by a greater homogeneity of the DG on the surface as well as throughout the interior of the membrane, since grafting was performed on powder substrate prior to film formation and the styrene has better access to the radiation-activated polymer. Weight percent water uptake of UHMWPE-g-PSSA was higher than Nafion. However, contrary to Nafion, the volume percent water uptake of the swollen UHMWPE-g-PSSA membranes was lower. Methanol permeability is in the range of $4.86 \times 10^{-8} \text{ cm}^2/\text{s}$ for a DG of 12% to $1.45 \times 10^{-6} \text{ cm}^2/\text{s}$ for a DG of 44% UHMWPE-g-PSSA. The methanol permeability of the membrane with a DG of 44% is surprisingly lower than that of Nafion $(1.65 \times 10^{-6} \text{ cm}^2/\text{s})$, even though it had higher swelling and this trend was followed up to the conductivity 0.227 S/cm, corresponding to a DG of 44%. Hence methanol transport is found to be influenced mainly by the kinetic factor (diffusion) instead of the equilibrium factor (sorption) for UHMWPE-g-PSSA membranes. TEM confirmed the presence of hydrophilic (grafted PSSA part) and hydrophobic (backbone UHMWPE part) regions within the UHMWPE-g-PSSA membrane. Thermal analysis shows the decomposition of sulfonic acid group starts ~260 °C. Physically, the membrane remained flexible for the entire DG range up to 58%, even after postsulfonation. The optimum DG for radiation-grafted UHMWPE membranes prepared in this study was found to be between 20% and 44%. Below 20%, conductivity is insufficient. Above 44%, the methanol permeability of the membranes increases undesirablv.

In summary, UHMWPE-g-PSSA membranes have lower methanol permeability than Nafion, while having acceptable to very high proton conductivity. Proton conductivity has a regularly increasing relationship with *DG*. These factors and film flexibility (non-brittleness) throughout the range of *DG* combine to make it a most promising alternative for Nafion for use in a low temperature hydrogen fuel cell and particularly for direct methanol fuel cell.

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