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 resulting membranes were 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 illustrated 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 within the magnitude of 10^{-3} Scm^{-1} and 10^{-2} Scm^{-1} at room temperature and at higher operating temperature, respectively.

Keywords : Pore-filled membranes; proton exchange membrane; electron beam radiation; physical and chemical properties

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,

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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 economically produced.

A new concept of ion exchange membranes has been developed in which a controlled amount of polyelectrolyte anchored within the pores of a porous membrane [5, 6, 7]. 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 will 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, limiting it's swelling, and provides mechanical strength for the membrane.

Previously, we have reported the preparation of sulfonated polystyrene pore-filled electrolyte PTFE membranes by using electron radiation grafting method [8]. Hence, in the this study, we reports the work done on the sulfonation of the styrene grafted membranes. The physico-chemical properties of the sulfonated polystyrene pore-filled electrolyte PTFE membranes such as water and methanol uptake, ion exchange capacity and ionic conductivity were investigated in correlation with the grafting yield.

2. Experimental

2.1. Materials and methods

The sulfonated pore-filled electrolyte PTFE membranes were prepared by the simultaneous method. The materials, such as monomer (styrene) and polymer substrate (PTFE film: 150μm thickness, density of 1.94g/cm^3, average pore size of 0.15μm) and the grafting and sulfonation procedures were described in detail in the previous study [8]. The other chemicals were reagent grade and used without further purification.

2.2. 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 hr, 80°C and 10^{-3} torr) and then over silica gel in an evacuated desiccator's for 1 hr. The samples (3 x 2 cm^2) were immersed in water or in methanol placed in a glass container at room temperature for up to one day. After immersion completion, 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:

$$WU = \frac{w_{wet} - w_{dry}}{w_{dry}}$$

(2.1)

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

$$\text{Hydration number} = \frac{w_x \left\{ M_{styrene} \left[1 + \frac{(GY)}{100} \right] + \left[\frac{(GY)}{100} \frac{(SY)}{100} M_{SO3H} \right] \right\}}{\left\{ M_x \frac{(GY)}{100} \frac{(SY)}{100} w_{dry} \right\}}$$

(2.2)

where w_x is the mass of absorbed water, w_{dry} is the mass of dry membrane, $M_{styrene}$ is the molecular weight of styrene, M_{SO3H} is the molecular weight of sulfonic acid group, M_x is the molecular weight of H_2O or CH_3OH, Gy is the grafting yield and SY is the sulfonation yield.

2.3.   Ion exchange capacity (IEC)

The ion exchange capacity [meq/g] of the membranes was determined by acid-base titration technique. The dried membrane samples (3 x 2 cm^2) 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 hours and washed free of acid. The membrane samples were then dried in vacuum oven (1 torr, 60°C) for overnight. The dry weight of the membranes was determined after keeping it in a desiccator at ambient temperature over fresh silica gel for 30 minutes. The ion exchange capacity (IEC) of the dry membrane per unit mass (meq/g) was calculated from the following relationship,

$$IEC = \frac{V_{KOH} \times 0.05}{m_{dry}}$$

(2.3)

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

The equivalent weight (EW) was calculated from the following equation [9-11].

$$E.\ W = \frac{1000}{IEC} \tag{2.4}$$

2.4. Conductivity

Prior to conductivity measurements the membranes have to be transformed into protonic or acidic form first. The proton conductivity of the membrane was measured with a LCR meter (Agilent HP 4284A) by using a frequency range of 20 Hz to 1MHz. The temperature range of the impedance studies was 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,

$$\sigma\ (\Omega^{-1}cm^{-1}) = \frac{L}{RA} \tag{2.5}$$

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

3. Results and discussion

Swelling behavior is regarded as one of the important characteristics for the sulfonated pore-filled polystyrene electrolyte membranes, which confirmed the successful incorporation of hydrophilic group inside the membrane. It is also determined the water and methanol uptakes capabilities that in turn related to the membranes electrochemical properties. 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 term of solvent uptake (water and methanol) and hydration number i.e. the number of water or methanol molecules per sulfonic acid group (H_2O/ SO_3H or CH_3OH/ SO_3H ratios).

The percentage of the solvent uptake (i.e. water and methanol) with various grafting yield is plotted in Figure 1. 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 uptakes increase from 7.28 to 32.07 wt% 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 the both solvent uptakes in all membranes can be reasonably attributed to the increase in the hydrophilicity imparted to the membranes 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 Yamaghuci et al. [7] and Nasef et al. [8]. Such expected

behavior is due to the effect of the suppression of the swelling by the porous hydrophobic PTFE matrix structure. The water uptake of Nafion 117 membrane was found to be about 20 wt % under the same condition conducted.

However, the water uptake values for these sulfonated membranes are 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 Figure 2. The hydration number is defined as the number of solvent molecules per sulfonic acid group (i.e. H_2O/ SO_3H or CH_3OH/ SO_3H ratios). It is observed that the hydration
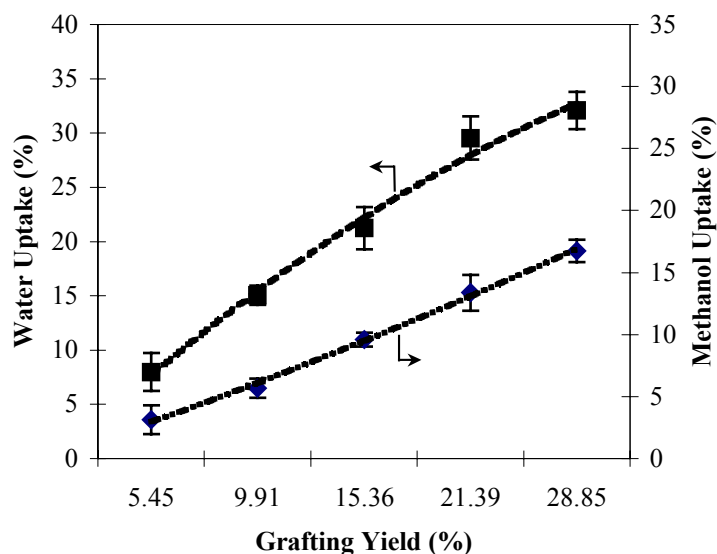
Figure 1: Water and methanol uptakes for sulfonated polystyrene pore-filled electrolyte PTFE membranes as a function of the grafting yield
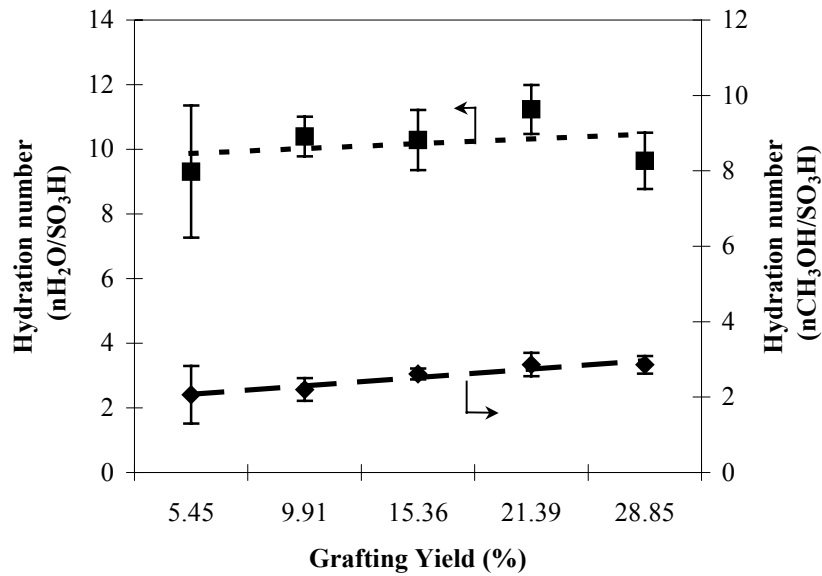
Figure 2: Variation of the hydration number in water and methanol for sulfonated polystyrene pore-filled electrolyte PTFE membranes as a function of the grafting yield

number is approximately 10 H_2O/SO_3H when the samples are equilibrated in water, and approximately 3 CH_3OH/SO_3H 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 to the fact that the mobilities of the sulfonated polystyrene grafts incorporated in the PTFE matrix are relatively sufficient in order to allow water penetrates easily throughout the membranes [12].

Figure 3 shows the extent of ion exchange capacity (IEC) and equivalent weight (EW) which expressed as the miliequivalent 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 increases 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 membranes pores in the form of gel type electrolyte, which provides interconnected hydrophilic cationic regions through the resulting membranes [8].

According to Büchi et al.,[13], the possibility to prepare 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.
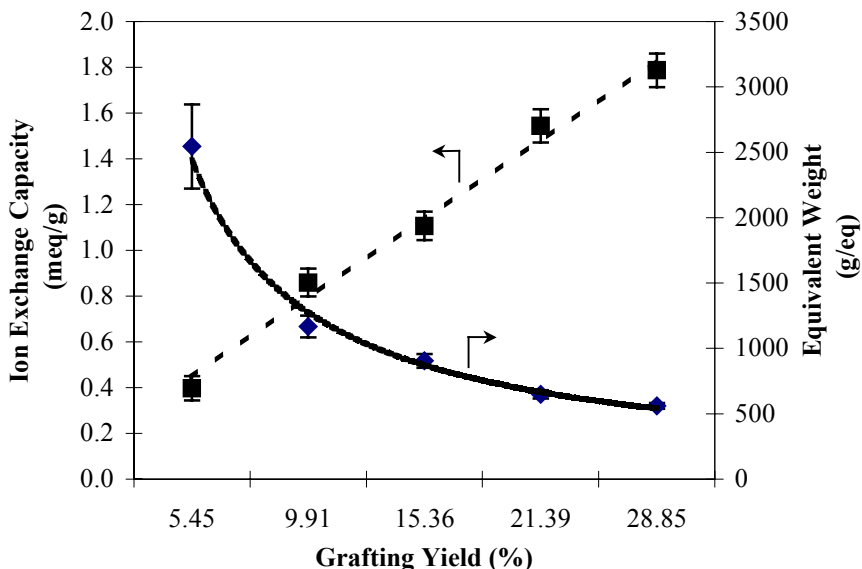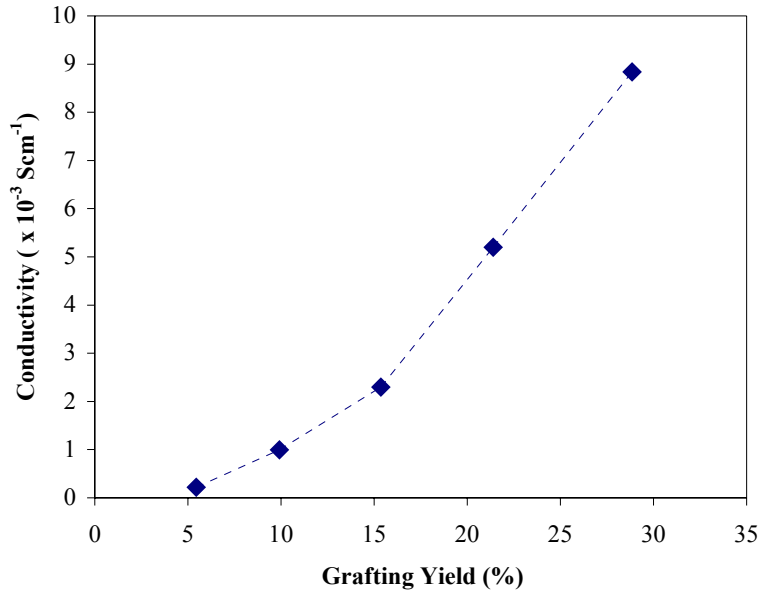

Figure 3: The relationship between ion exchange capacity (meq/g) as well as equivalent weight (g/eq) and grafting yield of sulfonated polystyrene pore filled electrolyte PTFE membranes.
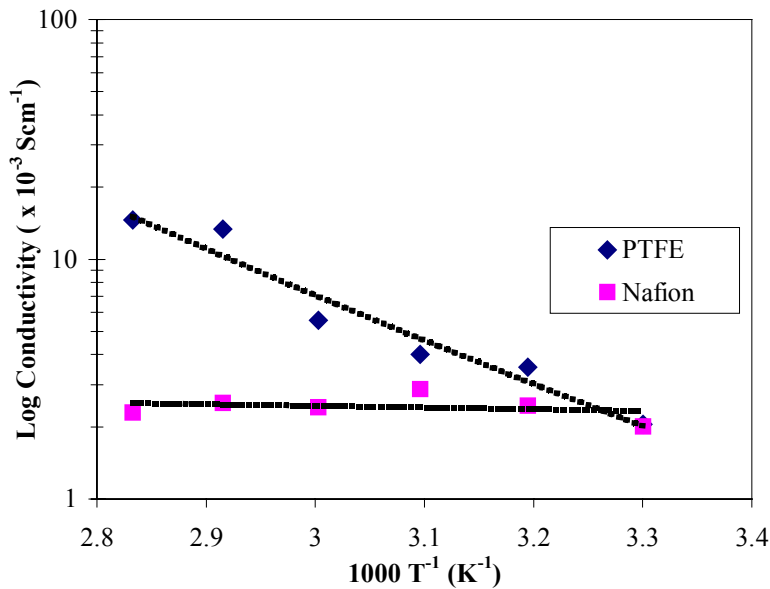
The proton conductivity of sulfonated polystyrene pore-filled electrolyte PTFE membranes with various grafting yields measured at room temperature is illustrated in Figure 4. Figure 4 showed that the proton conductivity increases as the grafting yield increases. The conductivity increases from 0.22×10^{-3} to 8.84×10^{-3} Scm^{-1} as the grafting yield increases from 5.45 to 28.85%. This can be understood on the basis that ionic conductivity is a function of IEC, solvent uptake and hydration number of the membranes were found to be strongly depends 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.

However, an abrupt increase in the conductivity with grafting yield is observed upon reaching a grafting yield of approximately 15%. At the grafting yield beyond the 15% is assumed to change the filled structure of the sulfonated polystyrene grafts content anchored within the membrane that leads to an increase in proton conduction region [7]. In other words, as the grafting yield increases beyond 15%, there is an increase in the number of sulfonic acid groups participated in the conduction process due to the changes in the polymer morphology, which perhaps owing to the alteration of the hopping distance between cluster zone. The respective conductivity value for Nafion 117 is found to be approximately 1.96×10^{-3} Scm^{-1}. The fairly decreased in Nafion's conductivity is suggested to be probably due to the incomplete regeneration into acidic form during the sample preparation.

Figure 5 displays the Arrhenius plot of the conductivity as a function of temperature for the sulfonated polystyrene pore-filled electrolyte PTFE membrane that 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 exhibit to increase as the operating temperature increases from 303 K to 353 K. As the ionic conductivity of electrolytes is

Figure 4: The relationship between conductivity and the grafting yield of sulfonated polystyrene pore-filled electrolyte PTFE membranes at ambient temperature.

Figure 5: Proton conductivity-temperature dependence of sulfonated polystyrene pore-filled electrolyte PTFE membrane having a grafting yield of 15.36 %.

in general 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 [14]. 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 according to the Arrhenius equation [$\sigma = \sigma_o \exp(-E_a/RT)$] is approximately 24 kJmol^{-1} and 0.411 kJmol^{-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 if the membrane is saturated with water formerly. Higher activation energy value indicates to the reduction in proton mobility within the membrane and vice versa [15].

4.   Conclusions

Investigation of the properties of the sulfonated polystyrene pore-filled electrolyte PTFE membranes such as swelling behavior, IEC and conductivity was carried out and it can be concluded that:

1.   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 also the hydration number (H_2O/ SO_3H) 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.

2.   It can be suggested that 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 expected behaviors is evident to the fact that with increasing grafting yield, progressively more sulfonic acid groups are incorporated within the resulting membrane.

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

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