

Grafting of Styrene onto Commercial PTFE Membrane and Sulfonation for Possible Use in Fuel Cell

E.E. Abdel-Hady¹, M.M. El-Toony^{2*}, M.O. Abdel-Hamed¹ and A.M. Hammam³

¹Physics Department, Faculty of Science, Menia University El-Menia City, Egypt

²National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt

³Ahmad El-Zomr Street, P.O. Box 29- Nasr City, Cairo, Egypt

Abstract

Commercial poly tetrafluoroethylene (PTFE) inserted in silica with ratio of 8% was chosen. Gamma irradiation was used for grafting of different ratios of styrene onto membrane in one and / or two steps. Monomers mixture of styrene and each of methacrylic acid or acrylic acid were used as binary monomers for grafting of such membrane to raise the grafting percent and aids proton conductivity. Sulfonation of the grafted membrane was performed for hydrogen proton conduction enhancement. Confirmations of the grafting and sulfonation have been achieved by FTIR investigation while Ion exchange capacity was studied as well. The mechanical properties of the grafted PTFE were tested by hardness tester while their thermal behaviors were investigated using thermal gravimetric analysis. It was found that maximum water uptake percent of the sulfonated membrane reached to 28% by weight. The proton conductivity of the prepared membranes were measured by AC impedance spectroscopic analysis, it was reached to $9.6 \times 10^{-3} \text{ Ohm}^{-1} \text{ Cm}^{-1}$ which is comparable to that of Nafion.

Keywords: PTFE membrane; Gamma irradiation; Silica; Monomers; Grafting; Sulfonation; AC impedance

Introduction

Current demands to improve PEMFC efficiencies and to reduce cost and complexity of the systems require operating temperatures above 100°C. The membranes must be designed to maintain high proton conductivity at these temperatures, preferably approaching 100 m.simon/cm, in combination with a high chemical and mechanical stability to endure fuel cell operation in excess of 5000 hours Current PEMFCs typically run at $\leq 80^\circ\text{C}$ because of the working temperature limitation of the materials (usually Nafion). The high cost of the PEMFC is partially due to the expensive perfluorosulfonic membranes, such as Nafion membranes. Therefore, it is necessary to develop an alternative membrane which is less expensive and has a high performance. One of the ways is by modification of the commercial films using the radiation grafting method [1–12]. Recently, the radiation-grafted membranes have been well reviewed [1–3]. The grafting can be initiated by high-energy irradiation using Gamma-rays, electron-beam and swift heavy ions. Binary monomers of styrene/divinylbenzene (DVB) have been widely used as the graft components. Other monomers, such as styrene derivatives and acrylic monomers have also been investigated [5–10]. The base film in the membrane functions as a hydrophobic host that constrains the membrane swelling in water and provides mechanical strength and dimensional stability. The requirements for new membranes are somewhat related to those of PEMFC, but with an additional factor that since the fuel supplied to the anode is in liquid rather than gaseous form, swelling and crossover by methanol fuel must be controlled. The high permeability of methanol fuel from the anode to the cathode (crossover) through the currently used perfluorinated sulfonic acid membrane (Nafion) and the sluggish oxidation kinetics of methanol at the cathode pose serious problems for the commercialization of DMFC technology. Applications in terms of their lower weight and volume compared with indirect fuel cells. Furthermore, DMFC attracted interest for mobile and domestic application thanks to low operating temperature, fast start-up, and the easiness of fuel storage and transportation [13]. In order to improve

the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the loss of fuel across the cell membrane, usually termed “methanol crossover”. DMFC systems are based on polymer electrolyte in the form of proton exchange membrane fuel cell (PEMFC). It offers simple and compact design as the methanol is fed directly into the fuel cell. In other words, a DMFC system does not require a bulky and heavy hydrogen storage system or a reforming subsystem. For the purpose of reducing methanol crossover in DMFC, many studies were reported; that includes sulfonated perfluorinated materials [14,15], sulfonated poly hydrocarbons [16–18], acid–base blends with a surplus of acid ionic groups [19–21], organic–inorganic composite materials [22,23], and polymer blends [24]. There has been considerable effort spent trying to reduce methanol crossover and to reach high proton conductivity. Membranes containing metallic blocking layers have been proposed [25], and organic–inorganic composite membranes containing Zr phosphonates. [26], Sn-doped mordenites [27], zeolites [28], and silica [29] have been investigated. The preparation of hybrid organic–inorganic composites has attracted much attention because such hybrids may show controllable physical properties, such as optical, electrical, and mechanical behaviors, by combining the properties of both organic polymers and inorganic compounds [30,31]. In these organic–inorganic hybrids, the inorganic minerals precipitate in situ in a regular manner in the organic polymer matrix, and a strong interaction between the organic polymer and inorganic mineral is expected to result in a hybrid with markedly improved mechanical properties.

*Corresponding author: M.M. El-Toony, National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt, E-mail: Toonyoptrade@yahoo.com

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In this work, grafting of commercial PTFE (hybrid membrane) by styrene and binary monomers with acrylic and / or methacrylic acid and sulfonation was further more carried out. Thermal, mechanical, and chemical characterizations of the grafted membrane were performed. Morphological studies of the grafted membranes were carried out using scan electron microscope. Ion exchange capacity and water uptake of the membranes was measured prior to AC impedance investigation for possible use of the prepared grafted membrane in fuel cell.

Experimental Approach

Materials

Commercial polytetrafluoroethylene film which inserted silica within its matrix, with thickness 120 μ were used, purchased from OPTCo, Egypt.

- styrene of purity 99.9% and Methacrylic acid of purity 99.8% were supplied by Merck, Germany, other chemicals such as solvents, alkali acids....etc., were reagent grade (Data shown as supplementary).

Polysulfone

Preparation of grafted membrane: The direct grafting method was used as a technique in which the polymer and monomer solutions were subjected to ionizing radiation (Gamma rays ^{60}Co dose rate 1.22 Gy/Sec.) in a glass ampoule. After graft copolymerization, grafted films were washed with bi-distilled water and extracted with hot water to remove excess reagent. The films dried in vacuum oven at 30-40°C for 2 hours and weighed. The degree of grafting was determined by percent increase in weight using the following equation;

$$\text{Degree of grafting\%} = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

Where W_o and W_g represent the weight of initial and grafted film respectively.

Grafting with two steps were carried out by repeating grafting process by the same condition on the same membrane. Each step were performed via irradiation to 20 KGy, this technique was used to avoid reaching to the polymerization dose of styrene while increasing the free radicals formation for PTFE film.

Sulfonation of grafted membrane: The sulfonation of phenyl group of styrene was carried out by soaking the grafted film in a mixture of chlorosulfonic acid and 1,2 dichloroethane with a ratio of 1:1 in ice bath for interval times (hours). The membranes were then washed with distilled water and dried in oven at 40°C [32].

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

Water uptake studies: Respective water uptake / swelling behaviors of different ratios of grafted membranes were studied in water. Put a pieces (2.5 x 2.5 cm) of membranes with known weight into glass ceiled ampoules filled with water for 24 hours. Swollen polymer was wiped off with tissue paper and then weighed immediately to know the swelling percent or water uptake percent, which was calculated as:

$$\text{Water uptake\%} = \frac{\text{Weight of swollengrafted membrane} - \text{Weight of drygrafted membrane}}{\text{Weight of drygrafted membrane}} \times 100 \quad (2)$$

Ion Exchange Capacity (IEC): 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 phenolphthalein as indicator. The IEC was calculated using the following equation:

$$\text{Degree of grafting\%} = \frac{W_g - W_o}{W_o} \times 100 \quad (3)$$

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.

AC impedance measurement: Proton conductivity measurements were of the sulfonated grafted 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 HIOKI LCR Hi-Tester, Model:3532, Japan. Each membrane sample was cut into sections 2.5 cm x 2.5 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:

$$\sigma = \frac{l}{RS} \quad (4)$$

where σ is the proton conductivity (in simon/cm), l is the distance between the electrodes used to measure the potential ($l=1\text{cm}$), S is the membrane cross-sectional surface area (membrane width x membrane thickness) for protons to transport through the membrane (in cm^2) and R is derived from the low intersection of the high frequency semicircle on a complex impedance plane with the $\text{Re}(Z)$ axis.

Scientific equipments

FTIR characterization: The functional groups of the grafted membrane were studied using Mattson 1000, Pye-Unicam, England.

Thermalgravimetric analysis

Shimadzu TGA -50, Japan, was used to characterize the thermal stability of the porous blend.

Scan electron microscope

Investigation and magnification of the polymer surface was carried out by SEM, JEOL-JSM-5400; Japan.

Calibration data:-Gain factor: 49.996 live time: 80 seconds.

Sample data

- Total spectrum count: 875722, live time 70 seconds
- System resolution: 173 ev
- Accelerating voltage: 20,00Kv.

Hardness tester

Samples of were cut for 2.5 x 2.5 cm for hardness test. The measurement was carried out according to (ASTM D2240, 2000) by

manual analogue instrument with pin produced termed Baxio, UK. The unit of hardness is expressed in (Shore A).

Gamma irradiation

Gamma irradiation was carried out by ^{60}Co gamma rays with a cylinder irradiation chamber. All irradiations were performed at ambient temperature (about 45°C at the chamber) and a dose rate of about 1.22 Gy/Sec.

Results and Discussion

Theoretical approach

Organic-inorganic composites represent a useful approach. interesting reviews [33,34] or presentations on the preparation of original high temperature-DMFC membranes arising from composites made of fluoropolymers doped with fillers or solid inorganic proton conductors (zirconium hydrogen phosphates, hygroscopic oxides, heteropolyacids, (HPA), phosphotungstic acid (PWA), etc.). These membranes were tested at temperatures up to 120°C under ambient pressure and up to 150°C under pressure of 3–4 atm.

Preparing organic/inorganic hybrid polymers is an interesting way to improve the thermal stability of membranes. Three alternatives are possible to incorporate silica into organic matrices.

- (i) formation of two interpenetrating network (organic and inorganic);
- (ii) elaboration of a silica gel by acidic catalysis around a polymeric film;
- (iii) 'copolymerization' of an organic monomer with a siliated derivative.

The use of polysiloxanes gives copolymers with lower T_g , increased thermal stability of the hybrid system and decreased methanol crossover. Silica particles increase the water retention and hence the protonic conduction at high temperature.

Jung et al. [35] have reported the synthesis of a Nafion w 115 / Silica composite membrane obtained via the sol-gel acidocatalyzed of tetraethoxysilane (TEOS) (equivalent weight 1100). The amount of TEOS impregnated in the membrane varied with the reaction time. It was noted that; the water absorption of the composite membrane increased with the silica content, while the proton conductivity decreased. The silica particles inhibited the proton transfer. The methanol permeability of that membrane was that of Nafion, and

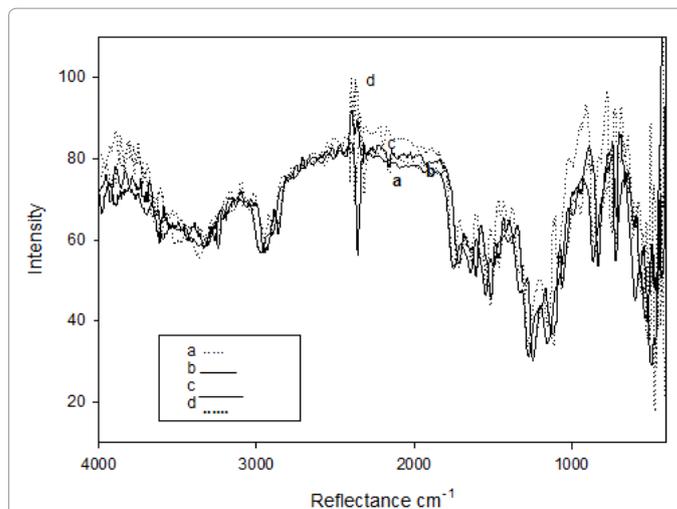


Figure 2 : Chart of FTIR of sulfonated (different sulfonation time) grafted styrene onto PTFE membrane, a) 1 h. sulfonation b) 2 h. sulfonation c) 3 h. sulfonation d) 4 h. sulfonation.

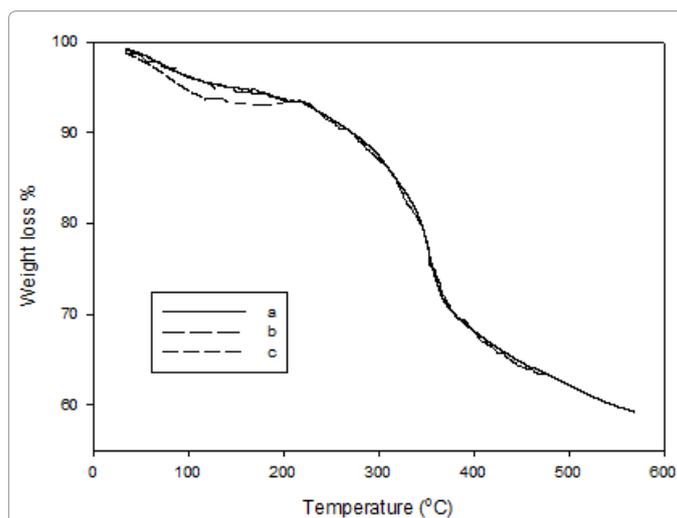


Figure 3: Thermogram of sulfonated (complete) styrene grafting PTFE with different grafting yield (15%, 22% and 31%).

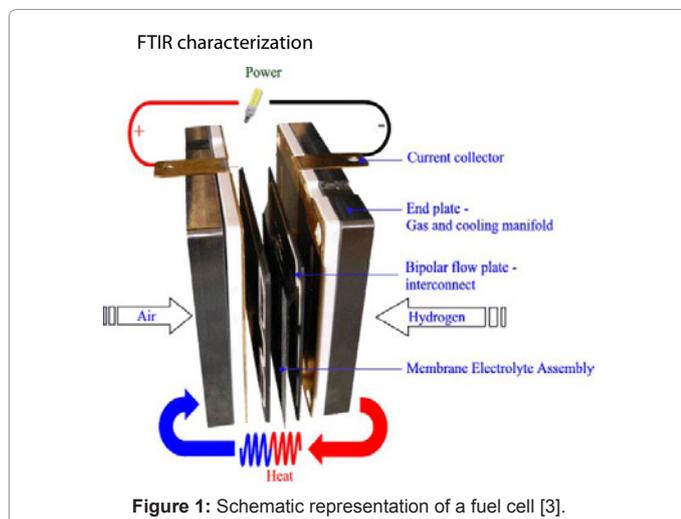


Figure 1: Schematic representation of a fuel cell [3].

the performance of the membrane in fuel cell improved up to a silica content of 12.4%, leading to potential applications in DMFC; for 0.5 V, the current density at 125°C was 650 mA cm^{-2} .

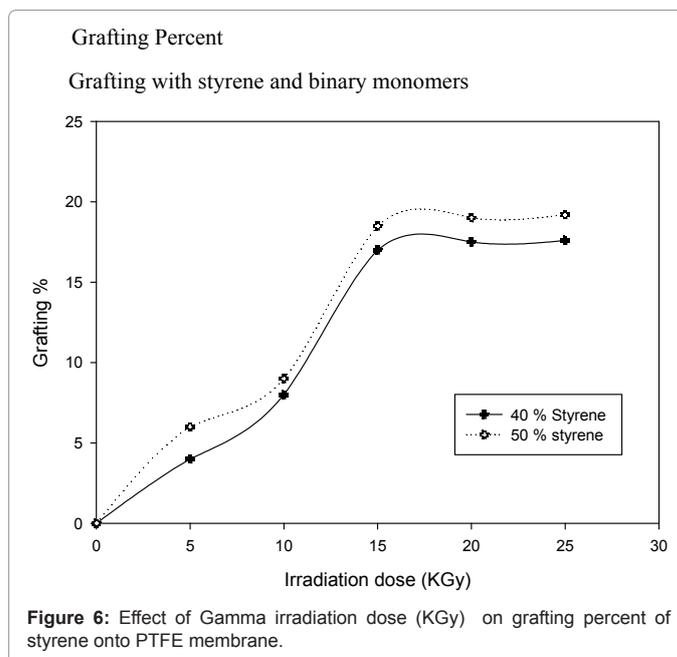
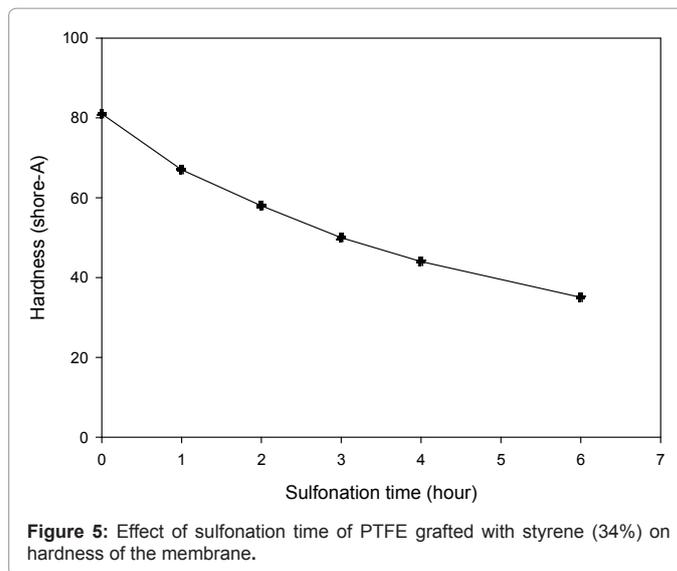
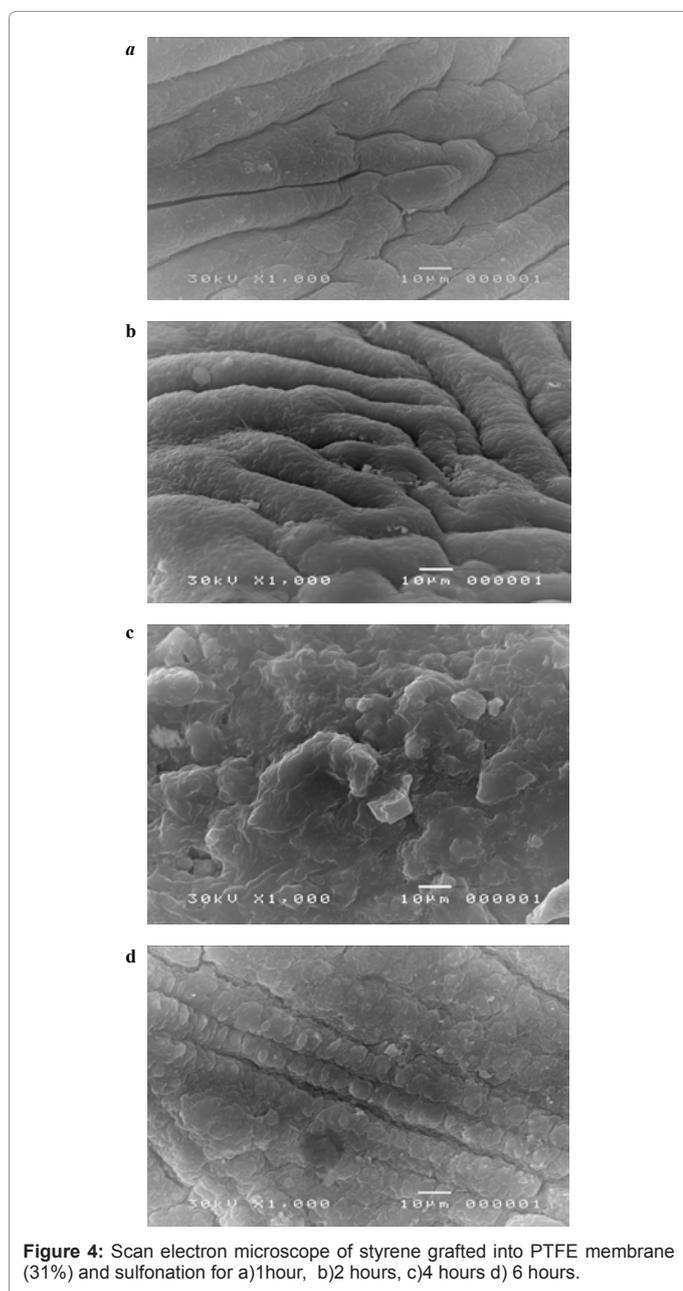
Characterizations of the grafted membrane

FTIR spectral analysis has been used to verify the incorporation of a PSSA moiety into the porous structure of the PTFE membrane and the formation of a polymer electrolyte membrane, as seen in Figure 2. comparison between a PSSA and its corresponding PS pore-filled PTFE and a pristine PTFE membrane clearly shows that the PTFE membrane 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%. Broad band may appear extend from 1007 to 1034 as seen in Figure 2d which also confirm the complete sulfonation, while intensity of peak

assure hydrophilicity of membrane which originate as long contact time between membrane and chlorosulfonic acid.

Thermogravimetric analysis

The thermogram could be divided into 5 divisions depending on similar behaviors of the attained results of the different grafting membranes' response by raising the temperature. First division showed a decrease in weight at low temperature with a nearly constant shape. This division has a wide range of temperature at 15% grafting percent, it decreased to 120°C with 22% grafting percent while it reduced to 100°C when grafting percent reached to 31%. Second division described a thermal stability through loss of weight did not exceed 5% for all understudied membranes. This division ranged (120-200°C) at 15% grafting percent, it widen for 22% grafting percent membrane to 150-200°C while it reduced for 31% grafting percent to a range of 100-



150°C. The third division described the convex thermogram regarding to temperature axe. These properties showed nearly same length of temperature (130-140°C), it started from 200-330°C for 15 and 22% grafted membranes while the range start from 150°C to 290°C for 31% grafted membrane. The fourth division described the abrupt change of weight loss which showed an obvious different changes. The range of this division has a constant range (200-330°C) corresponding to 15 and 22 grafting percent of the membranes. While this range widen include a range of 290-400°C. Through this division loss of weight for the thermograms are nearly constant (30% loss of weigh for 15% grafted membrane, 33% loss of weight for 22% grafted membrane and 35 % loss of weight for 31% grafted membrane). These results attempt on a less thermal stability upon raising grafting percent. The fifth division showed a low rate of weight loss in a range of 400 to 580°C. Loss of weight was nearly constant which was about 40% (41% loss of weight for 15 grafted membrane, 41% loss of weight for 22% and 31% grafted membrane).

Scan electron microscope

Grafting percent and furthermore sulfonation affect severely on the PTFE membrane morphology. Surface area increased with sulfonation time from 1 to 6 hours, grooves and channels are seen while it widens as it seen in Figure 4a and Figure 4b. further sulfonation conduct opening these channels in different positions leading to facilitation of ion transfers through the pores originates as complete sulfonation. Distribution of pores through the membranes surface area homogenously as seen in Figure (4c). Degradation of the membrane is noticed in maximum form in Figure d while maximum surface area is seen as well which confirmed the less mechanical properties as shown in figure (4d).

Hardness investigation

The membrane used in fuel cell acts as a carrier for proton transport and as a barrier to provide effective separation between the anode and cathode. The former requires the membrane to be as thin as possible, while the latter requires the membrane to be strong enough to avoid damage during the membrane electrode assembly (MEA) fabrication, and during the fuel cell operation. Especially in a DMFC, one side of the membrane is exposed to the liquid methanol solution, and the other side is exposed to the dry gas. Different swelling on the two sides will accelerate the degradation of the fuel cell membrane. In many cases, it is found that the degradation of the fuel cell is not only caused by the lower chemical stability, but by mechanical damage.

Evaluation of the mechanical properties of highest value of grafting (34 %) of the styrene grafted membranes have been evaluated. Hardness measurements showed decrease their value by increasing the contact time of sulfonation. Regular decrease of hardness was noticed in Figure 5 by sulfonation's contact time. As it is seen 6 hours is severely affected the hardness of the membranes which reached to half its value at zero contact time. So 3 hours contact time is recommended to be used while it performed nearly complete sulfonation.

Irradiation dose on the grafting yield was studied in the range of 5–25 kGy at constant 5 kGy per pass. As shown in Figure 6, the grafting yield increases gradually with the increase irradiation dose. This can be explained by the fact that; with the increasing the irradiation dose, the production rate of radicals' formation within the grafting system

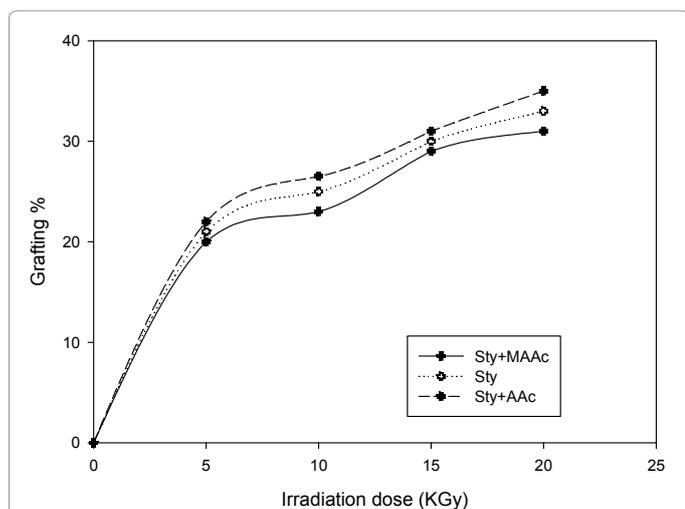


Figure 7: Effect of Gamma irradiation dose (KGy) on grafting percent of binary monomers onto PTFE membrane.

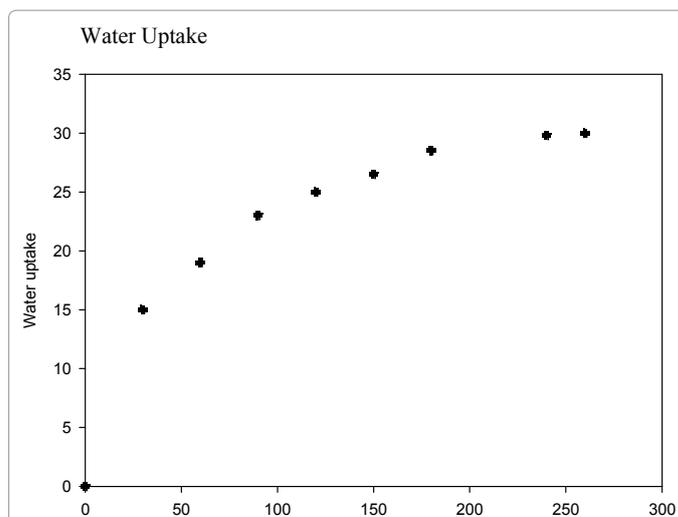


Figure 8: Effect of sulfonation time on water uptake of styrene Grafting PTFE membrane.

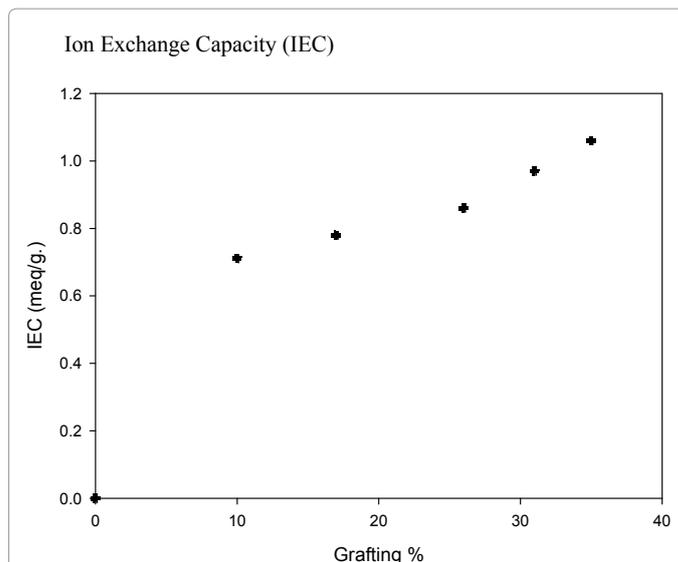


Figure 9: Effect of grafting % on ion exchange capacity of styrene grafted PTFE and sulfonation for 4 h.

was increased. Therefore, more radicals are available to take part in the monomer impregnation copolymerization reaction that consequently increases the grafting yield of the resulting membrane to a certain value after which it became constant. These results coincide with the result of previous researchers, who found that the grafting yield could be controlled by varying the irradiation dose [36-38] 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, 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 so it can repeat the grafting by the same condition on the same membrane after washing and drying to avoid polymerization of styrene (homopolymer formation). While further irradiation on PTFE membrane conduct more free radicals formation which raise up the degree of grafting. Binary monomers used raise up grafting percent as monomer add enhance grafting of the main monomer (styrene). Acid add (acrylic acid, methacrylic acid) stimulates graft yield increase comparing to single monomer grafting [39] as seen in Figure 7. Acrylic acid raise grafting onto PTFE more than methacrylic acid which is may due to low molecular weight leading to good chance to reach membrane's reaction zone. This finding is relatively in agreement with the results of Zhi-Li et al. [40], who studied the radiation graft

copolymerization of vinylimidazole (VI) onto PTFE films, respectively.

An increase in the water uptake of membranes with the increase in the degree of grafting and furthermore sulfonation was observed in Figure 8. The non cross-linked membranes have been also studied [41]. The increase in swelling corresponds well with the higher content of sulfonic acid groups with the increase degree of grafting, which in turn increase the membranes hydrophilicity. The water uptake increased with sulphonation till 90 minutes (contact time) at which water uptake value were 22 %. Rising up the contact time leads to gradual increase of water uptake till reach to 28% after 260 minutes.

The ion exchange capacities were determined by acid-base titration and are plotted in Figure 9. It was found that the ion exchange capacity increases with an increase in the degree of grafting, and is independent of the nature of the base films Below a 25% degree of grafting, it was found that each aromatic group of the graft chains is attached to one sulfonic acid group, and thus the obtained degree of sulfonation is close to 100%. However the value of IEC is over 25%, clearly deviated of the theoretical value. Even then, the degree of sulfonation is greater than 85%. Therefore, the ion exchange capacity could be freely controlled by changing the degree of grafting

AC Impedance

Figure 10 showed the Cole-Cole plot (Nquist plot) of styrene grafted PTFE at 300 K. The plot shows a high-frequency semi-circle and a low frequency spike for DG. It was reported [42] that, the high-frequency semi-circle is due to the parallel combination of bulk resistance, because of protons migration, and bulk capacitance, due to immobile polymer chains. The bulk resistance can be calculated from the intercept of low-frequency spike or of high frequency PSSA grafted membranes versus the grafting yield are presented in Figure 11 together with that for a Nafion 117 membrane. The ionic conductivity increases with increase in grafting %. Membranes with values of 19% grafting and above record an ionic conductivity as high as 10^{-3} simon cm^{-1} . The threshold ionic conductivity value is given by the membrane with grafting of 35%, viz., 9.6×10^{-3} simon cm^{-1} . This ionic conductivity is comparable to that of a Nafion 117 membrane, which was found to be 5.3×10^{-2} simon cm^{-1} under the same experimental conditions. The dependence of the ionic conductivity of PSSA membranes on the grafting yield (Y%) presented in Figure 8 is probably caused by the increase in both sulfonic acid groups associated with the amount of the sorbed water. This indicates that the incorporation of more PSSA provides a better environment for ionic mobility in these polymer membranes. 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., $Y = 30$ and 35% , suggests that the water swollen ionic domains in the membranes 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 (34%), the ionic domains become more interconnected and reach a percolation threshold beyond which diffusion limitations are overcome and allow the ionic conductivity to reach a maximum value.

Conclusion

This work has been performed for the purpose of synthesis of new membranes have low cost and availability for using in a fuel cell application. A hybrid commercial fluorinated membranes (poly

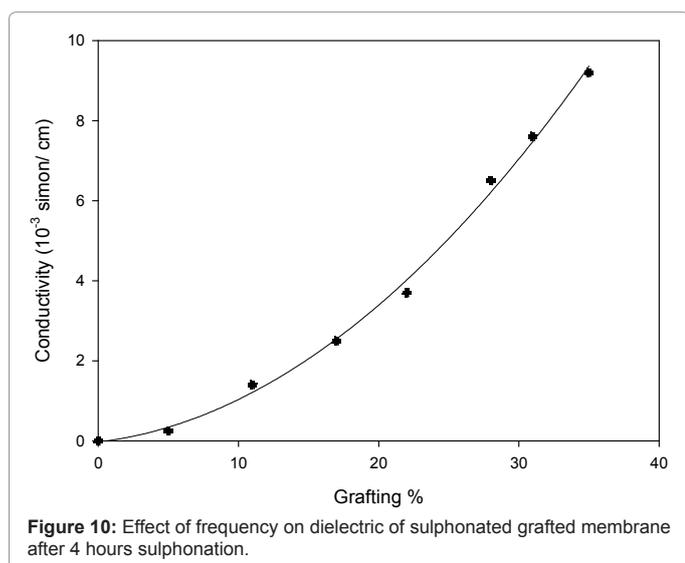


Figure 10: Effect of frequency on dielectric of sulphonated grafted membrane after 4 hours sulphonation.

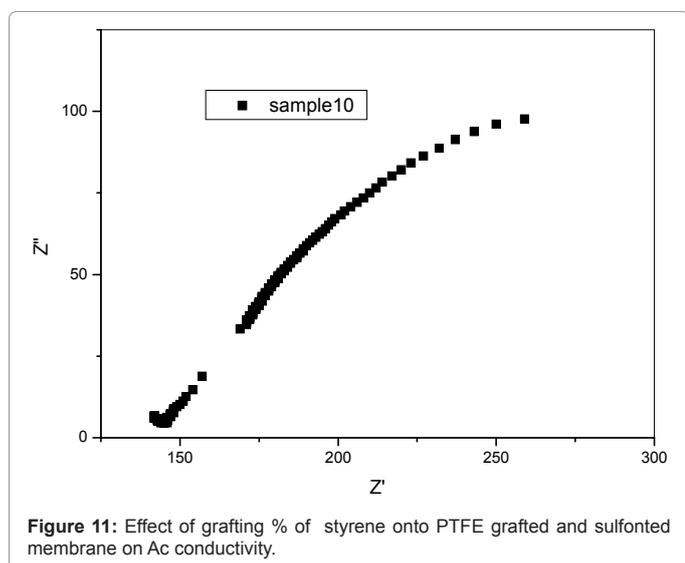


Figure 11: Effect of grafting % of styrene onto PTFE grafted and sulfonated membrane on Ac conductivity.

tetrafluoroethylene is inserted through silica with 8% by weight) were used. Simultaneous gamma irradiation proved to be effective tool for grafting styrene into the PTFE membranes. FTIR confirmed the grafting with different yields and sulfonation has been done as well. Ion exchange capacity was evaluated while the membrane hardness approved their durability. Characterization of the membrane including morphological properties, thermal behavior and water uptake have been carried out. Electrical investigation of the grafted membrane confirmed their usage in fuel cell as their value (nearly 1×10^{-2} simon/cm) is comparable to that of Nafion (5.3×10^{-2}).

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