

Application of Poly (Tetrafluoroethylene) Grafted with Styrene/Acrylic Acid for Proton Exchange Fuel Cell

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GAMMA irradiation was used effectively for grafting styrene and ... acrylic acid onto commercial poly (tetrafluoroethylene) (PTFE) films with 0.5% alumina nano-particle. It was found that; 40 KGy was the optimum dose to attain the maximum grafting yield when the monomers ratio was 60% styrene: 40% acrylic acid. The prepared membranes are characterized using FT-IR, tensile strength and scanning electron microscopy. Some parameters such as water uptake, ion exchange capacity and proton conductivity were determined in order to examine the membranes capability for the fuel cell application. The free volumes sizes were evaluated using positron annihilation lifetime spectroscopy (PALS). Fuel cell performance based the highest grafted yield membrane was tested onto proton exchange membrane fuel cell (PEMFC). The membrane proved their applicability up to 450 hr that recommend their utility from the cost benefit point of view.

Keywords: Grafting, Characterization, Positron annihilation, Fuel cell, Durability.

Proton exchange membrane fuel cell (PEMFCs) is one of the most attractive power sources for different applications, due to its reasonable operating temperature and high power density compared to other fuel cell types⁽¹⁻³⁾. These issues include thermal and water management during the operational process, as well as the membrane electrode assembly (MEA) reliability and durability. Among these concerns, water management stands out as one of key challenges in commercialization process, because it plays a critical role in protons transport and reactant gases in the porous electrodes⁽³⁻⁵⁾. PEMFCs are typically made using a hydrated polymer electrolyte membrane (PEM), such as Nafion 212 membranes, due to their favorable chemical and mechanical stabilities along with their high proton conductivity in the hydrated.

Poly (tetrafluoroethylene) (PTFE) and related fluoropolymers have excellent mechanical properties, even under very harsh conditions⁽⁶⁻⁹⁾. Over the recent

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years, more and more research has been carried out on the poly (tetrafluoroethylene) membranes functional modification using gamma irradiation technique⁽⁹⁻¹¹⁾. Novel cation exchanger membranes were prepared by simultaneous gamma irradiation for acrylic acid and styrene grafting onto poly (tetrafluoroethylene) and furthermore sulphonation was carried out in order to be applied as proton exchangers⁽¹¹⁻¹³⁾.

Hybrid organic–inorganic membranes are characterized by incorporation nanometric scale of an inorganic solid (filler) into an organic polymer serving as the matrix component⁽¹⁴⁾. In a hybrid system, the filler–polymer interaction can range from strong (covalent, ionic) bonds to weak physical interactions. In the last decade, several studies have reported on consistent improvements (membranes reinforcement, control the H⁺ and gasses passage) the PEMFCs performance by inorganic nanoparticles insertion, such as metal oxides (alumina), into the polymeric membrane^(15, 16).

The membranes showed better mechanical properties than Nafion 212 and generally exhibit satisfactory proton conductivity at high ion exchange capacity values (*IEC*). Such a high *IEC* generally leads to excessive water swelling and higher electrical conductivity. However, one of the main technological problems of the PEMFC is the lifetime limitation under typical operating conditions, even under operation with pure hydrogen. The fuel cell durability targets exceed 5000 hr for automotive applications and 40,000 hr for stationary applications^(17, 18).

Aim of the work

The work aims at preparing cheap membranes for generating environmentally friend energy via PEMFC technology. It includes grafting of such hybrid low cost poly (tetrafluoroethylene) (with 0.5 alumina nanoparticles) with acrylic acid and styrene using gamma irradiation as a facilitating tool. Sulphonation of the grafted membranes was carried out and further sulphonation was attained in order to improve their characteristics in the proton exchange membrane fuel cell applications. The membranes characterizations were performed using FTIR, scanning electron microscopy and some impacts such as water uptake, ion exchange capacity, AC electrical conductivity, pore size and tensile strength were evaluated to examine their availability into proton exchange membrane fuel cell. Polarization curves proved the membranes applicability into the fuel cell compared to Nafion112. The membranes durability recommend their utility into the desired application (upto 450 hr) from the cost benefit point of view.

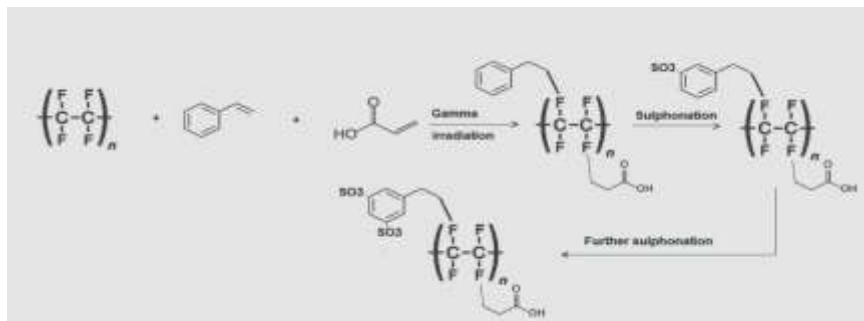


Fig. 1. The work flue chart 2.

Experimental Data

Materials

Poly(tetrafluoroethylene) (PTFE) films of 50 μm thickness possessed nano alumina particles (up to 75 nm) with 0.5% by weight were supplied by Optco, Egypt. It was cut into 5 X 5 cm^2 size and washed with methanol to remove any impurities cohering to the surface. The films were dried under vacuum at room temperature before their usage for grafting process. Gamma irradiation was carried out using Co-60 gamma radiation source. Styrene was purchased from Merck, Germany while acrylic acid and chlorosulfonic acid were purchased from Aldrich, England. 1,1,2,2-tetrachloroethane and different solvents were supplied by El-Nasr Co., Egypt.

Membrane preparation

The simultaneous radiation grafting was carried out by putting the poly(tetrafluoroethylene) films with 0.5 % nanoparticles alumina in two cm diameter glass ampoules. Mixtures of acrylic acid and different ratios of styrene with their solvents were added to the glass ampoules content. The ampoules were subsequently irradiated for different doses (5, 10, 20, 25, 30, 40 and 50 KG). After the grafting reaction, the films were taken out, rinsed with toluene and left soaked overnight to remove homopolymer. After drying to a constant weight, the grafting degree was obtained as follows:

$$\text{Grafting degree} = \frac{W_g - W_o}{W_o} \times 100 \dots\dots(1)$$

where W_o and W_g are the weight of un-grafted and grafted films, respectively.

Membranes sulfonation

Polystyrene grafted poly(tetrafluoroethylene) membranes were initially washed with dichloromethane, soaked therein for 30 min and then removed and dried in a vacuum oven for 1 hr. The films were then sulfonated using a

sulfonation mixture composed of 20% chlorosulfonic acid and 80 % 1,1,2,2-tetrachloroethane. The sulfonation was performed in a glass reactor containing both the films and sulfonation mixture, while the reactor temperature was maintained at 25 °C (ambient temperature). The sulphonation yield can be raised up by increasing the sulphonation time, increasing the chlorosulphonic acid concentration. While repeating the sulphonation process can increase the sulphonation yield larger than 100%. The sulfonation reaction was allowed to continue for 4 hr.

Sulfonated polystyrene electrolyte membranes were then removed and rinsed thoroughly with 1,1,2,2- tetrachloroethane, dichloromethane and tetrahydrofuran in order to remove the excess of chlorosulfonic acid. The obtained membranes were then hydrolyzed with 0.5 M KOH solution overnight and regenerated by boiling with 1 M HCl for several hours. The membranes were then washed with deionized water in order to ensure complete removal of acid, and finally stored in sealed bottles at ambient temperature⁽¹⁹⁾.

Ion exchange capacity (IEC) and degree of substitution

IEC of the sulfonated polymers was measured using a typical titration method. The dried membranes in the protonic form were immersed into 25.00 ml of 3 M NaCl solution for 24 hr. A large excess of Na⁺ in the solution ensured ions exchanging was nearly completed. Then, 10.00 ml of the 3 M NaCl solution containing the released H⁺ was titrated against 0.05 M NaOH solution using phenolphthalein as indicator. The IEC was calculated using the following equation:

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

where V_{NaOH} (ml) is the volume of 0.05 M NaOH solution used for titration. *n* is the factor corresponding to the ratio of the NaCl solution amount 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 membrane in the protonic form⁽²⁰⁾.

Water uptake and proton conductivity

The water uptake was measured by immersing the membranes in deionized water and weighted several times until no further weight change was observed. The equilibrium water uptake weight was determined as the following:

$$\text{water uptake} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100 \dots\dots\dots(3)$$

where W_{wet} and W_{dry} are the membranes weights in the wet and dry states, respectively.

Proton conductivity was determined by impedance spectroscopy measurement using a LCR meter, Herioki, Japan using a frequency range of 20 Hz to 1 MHz. The samples were hydrated in deionized water at 25°C (ambient temperature) overnight before the measurements. The high frequency intercept on the real axis of the Nyquist plot was used to calculate the membrane proton conductivity. The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma (\Omega^{-1} \text{cm}^{-1}) = \frac{L}{RA} \dots\dots\dots(4)$$

where L is the membrane sample thickness, A or (πr^2) is the sample surface area and R is the electrical resistance⁽²¹⁾.

Positron annihilation lifetime spectroscopy

The positron annihilation lifetime (*PAL*) spectra of the membranes were determined by detecting the prompt Y-ray (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ²²Na radioisotope and the subsequent annihilation Y-rays (0.511 MeV). A conventional fast-fast coincidence circuit of *PAL* spectrometer with a time resolution 240 Ps was used to record all *PAL* spectra. The *PAL* spectra containing 1.5 x10⁶ counts were analyzed into three lifetime components (T_1 , T_2 , and T_3) and their intensities (I_1 , I_2 and I_3) using *PALS* fit program⁽²²⁾.

Fuel cell performance

The membrane electrode assemblies (MEAs) were fabricated by hot pressing the anode and the cathode to the membrane at 130 °C for 2 min with 3 tons force. The Pt loading in the anode and the cathode were 0.3 and 0.5 mg /cm², respectively. The active area of MEAs was 5 x 5 cm². The MEA was placed in a single cell using (Pt/C) as the end plates and stainless mesh as the current collectors. The prepared grafted membranes were examined at 80 °C temperatures while the single cell was kept running with dry H₂ and O₂. Pure hydrogen and oxygen or air were used as fuel and oxidant with a flow rate 0.2 L / minute regulated by a mass flow controller (Brooks). The MEAs were evaluated with a commercial fuel cell test systems (Compucell, GT, Electrochem) and a single cell test rig. After stable cell performance was maintained the cell voltages and power densities at different current densities were recorded⁽²³⁾. The membranes were treated by boiling in 3% H₂O₂, 0.5 M

H₂SO₄ and deionized water to completely remove all impurities before experiment has been carried out ⁽²⁴⁾.

Scientific equipments

FTIR characterization

The functional groups of the grafted membranes poly (tetrafluoroethylene) grafted with styrene and acrylic acid) were studied using Mattson 1000, Pye-Unicam, England.

Scanning Electron Microscopy (SEM)

Investigation and magnification of the grafted membranes' poly (tetrafluoroethylene) grafted with styrene and acrylic acid) surfaces were carried out by scanning electron microscope (SEM), JEOL-JSM-5400, Japan. The magnification was 30 KV X1000.

Tensile measurements

Five individual dumbbell-shaped specimens were cut out from the grafted membranes [poly (tetrafluoroethylene) (PTFE) grafted with styrene and acrylic acid] using a steel die. The minimum thickness of the test specimens was determined by micrometer. A bench mark of 1.5 cm was made on working test specimen parts. The ultimate tensile strength was determined on a membranes tensile testing machine (Instron Machine model 1195, England).

Gamma irradiation

The dose rate used was 2.303727 kGy/h. The dose rate to water in the sample holder center of Russian Gamma Cell was calibrated by the National Physical Laboratory (NPL) in the UK using the alanine dosimetry system according to the standard **ISO/ASTM 51261 (2004)**.

Results and Discussion

Factors affecting grafting

Effect of monomers ratios and gamma irradiation dose

The effects of the monomers concentration ratio and gamma irradiation dose on the grafting degree of styrene and acrylic acid onto poly (tetrafluoroethylene) films with 0.5% nanoparticles alumina are shown in Fig. 2 and 3, respectively. The grafting degree increased with the increase in the monomers concentrations due to their higher concentration at the grafting sites. With the increase in the gamma irradiation dose (kGy), the grafting sites on the membranes increased and so higher graft yields were obtained. However, higher monomer concentration could cause more homo-polymers and lower grafting efficiency. Large values of radiation doses could damage the mechanical properties of poly (tetrafluoroethylene) membranes. In this

study, the obtained results were the optimal monomers' concentration ratio was 60% and 40% styrene and acrylic acid, respectively. While 40 KGy was the optimum gamma irradiation dose for attaining the highest grafting yield.

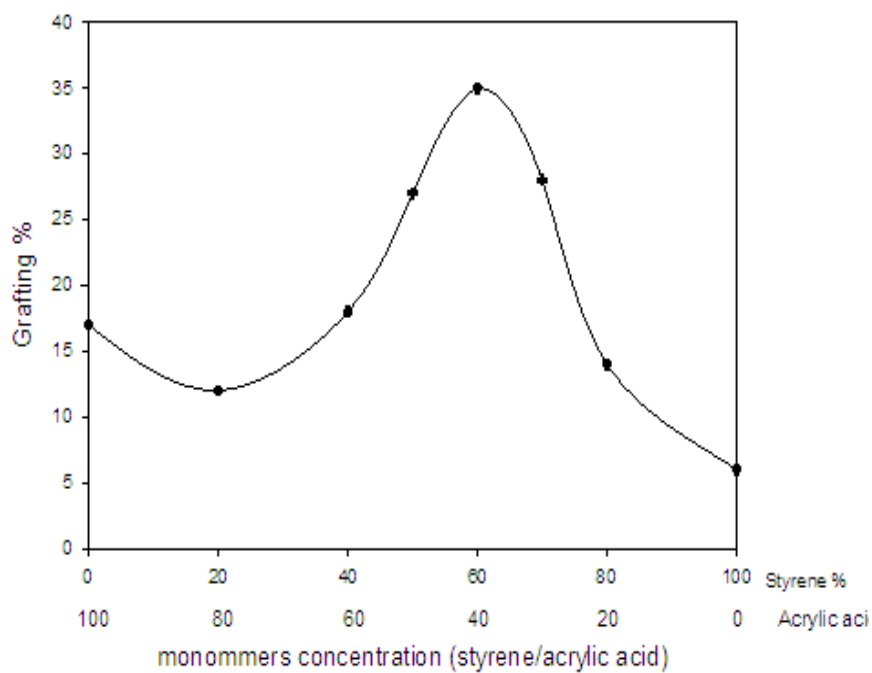


Fig. 2. Effect of monomers (styrene and acrylic acid) concentrations ratio on the grafting yields onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes at 40 kGy gamma irradiation dose.

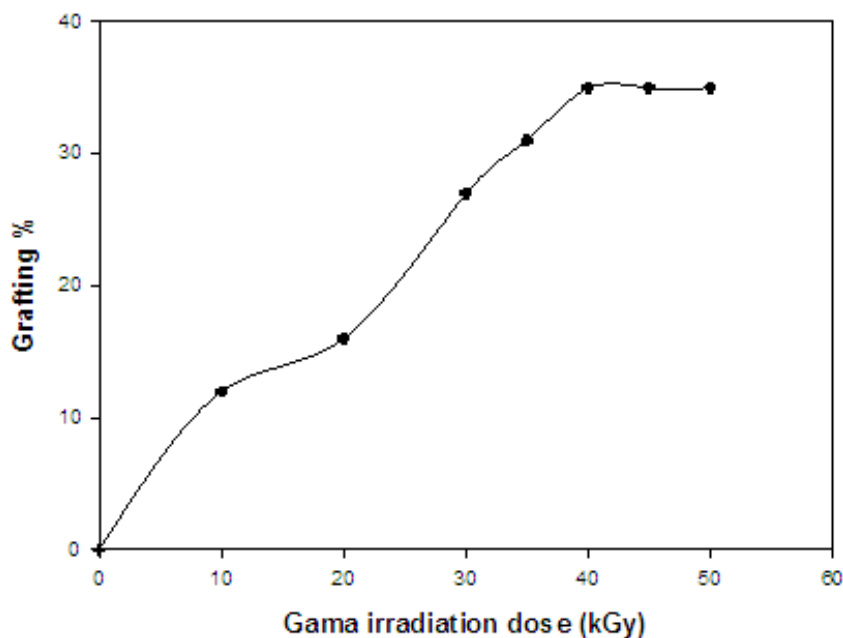


Fig. 3. Effect of gamma irradiation (kGy) dose on the grafting of monomers (styrene and acrylic acid) onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes at 40 acrylic acid: 60 % styrene ratio.

Grafted membranes characterizations

FT-IR characterization

Typical fourier transformer infrared (FT-IR) spectra of the grafted poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes having various degrees of grafting with styrene and acrylic acid were shown in Fig. 3 and 4. The characteristics bands at $1150\text{--}1250\text{ cm}^{-1}$ were assigned for CF_2 stretching vibration at poly (tetrafluoroethylene) membrane. The benzene rings in polystyrene graft was established by the $=\text{C-H}$ stretching vibration at 3050 cm^{-1} . While skeletal C=C in-plane and stretching vibrations were noticed at 1500 cm^{-1} and 1600 cm^{-1} , respectively. The benzene ring mono-substitution was confirmed by the aromatic out-of-plane C-H deformation band at 860 cm^{-1} . The absorption bands at $2800\text{--}2900\text{ cm}^{-1}$ and $2900\text{--}3000\text{ cm}^{-1}$, were assigned to symmetric and asymmetric stretching aliphatic CH_2 groups, respectively. The polystyrene characteristic bands intensities reflected the difference in the grafting yields⁽²⁵⁾. The absorption bands at 3400 and 1720 concerning to acrylic acid were identified corresponding to the OH and C=O stretching bands, respectively⁽²⁶⁾. These results confirmed grafting acrylic acid and styrene onto poly (tetrafluoroethylene) membranes.

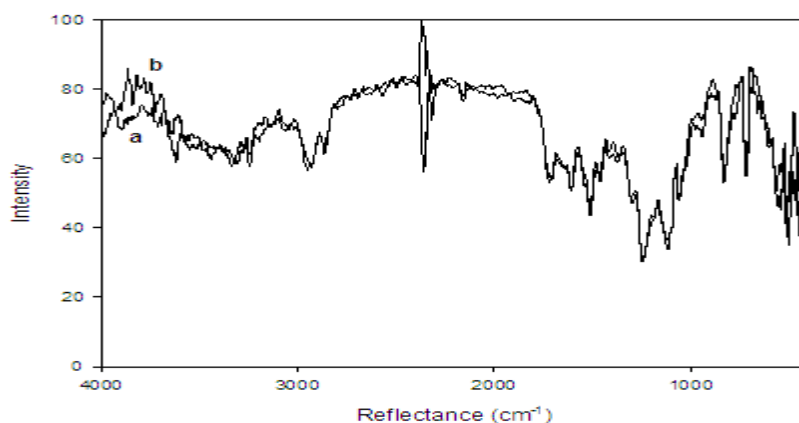


Fig. 4. FT-IR chart of styrene and acrylic acid grafted onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes.

- a) 16% grafting yield.
- b) 27% grafting yield.

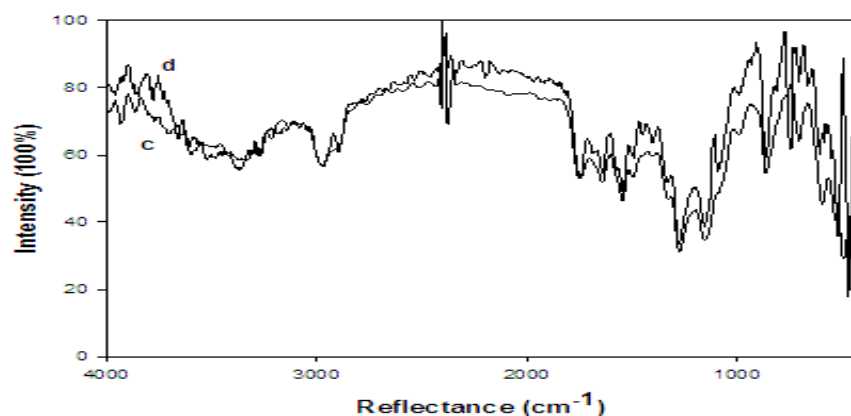


Fig. 5. FTIR chart of styrene and acrylic acid grafted onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes.

- c) 36% grafting yield.
- d) 44% grafting yield.

Scanning electron microscopy

Figure 6 (a-e) showed morphological properties of the grafted membranes [poly (tetrafluoroethylene) with 0.5% alumina nanoparticles grafted with styrene and acrylic acid] with different yields.

Figure 6(a) showed dark matrix without any changing in color. No dots, spots or channels were seen. It was attributed to no grafting has been

performed. Figure 6(b) showed white small dots and very narrow channels distributed onto black matrix zones. Less dark zones have been noticed alternating with the darker one. These illustrations were attributed to the less grafting yield (16%). Figure 6(c) showed an increase in the small dots number while appearing white spots with relatively large circumference distributed onto the polymer matrix. Small and excess numbers of channels with different directions were noticed. These observations ensured that larger grafting percent (27%) has been performed. Figure 6(d) showed deep, predominant, parallel and excess channel numbers while small ones were noticed with different directions. Whitish and grayish spots distributed onto the surface matrix have been noticed. These results were due to attaining a high grafting percent (36%). Figure 6(e) showed some cracks irregularly distributed onto the polymer surface. Obvious small channels with different directions observed may be due to starting degradation of the grafted membranes. Many white spots and whitish ones irregularly arranged were attributed to the highest grafting percent (44%) happened.

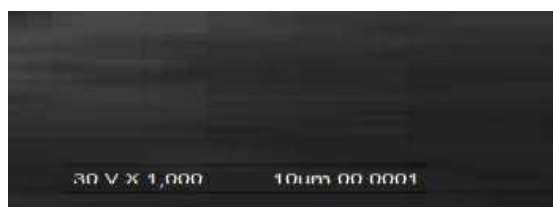
Characterizations the membranes for the fuel cell application

Table 1 tabulated many membranes properties such as water uptake, ion exchange capacity, proton conductivity, free volumes and tensile strength.

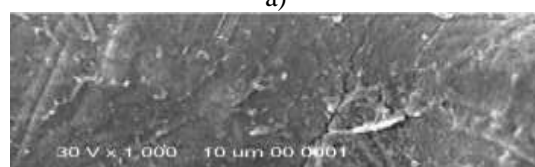
These parameters were intimately related to grafting yield of styrene and acrylic acid onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes. As well known, the proton affinity of water in forming hydronium ions played a significant role in the proton exchange process between different groups. Water could act as the carrier and medium for H^+ transport. However, membranes containing excessive water could lead to a decrease in mechanical strength and a dimensional mismatch when assembled into the fuel cell. The membranes hydration levels had a profound effect on the conductivity and mechanical properties. Accordingly, the preparation of sulfonated polymers with proper water uptake was crucial to obtain high performance for proton exchange membrane fuel cell (PEMFC) applications.

Higher temperature resulted in higher water uptake, ion exchange capacity and proton conductivity. The soft segments improved the molecular chains stretching up to 80 °C in the presence of water and the uncoiling chains would lead to absorption of more water and, hence, water swelling⁽²⁷⁾. But at ambient temperature the effect of uncoiling molecular chains was not obvious. So, the understudied membranes were recommended to be used onto the fuel cell at 80 °C. Positron annihilation lifetime spectroscopy is an important method for studying sub-nanometer free volumes sizes and for determination of the free volume fractions^(28, 29). Increasing grafting yield and furthermore sulfonation revealed increase in the membranes free volumes. Further sulphonation can raise their yield up exceeding 100%. It raised up to 149% at 44% grafting yield while it increased to 170% at the lowest grafting

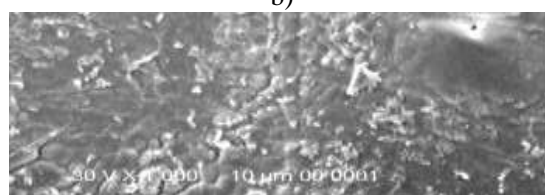
yield (16%). The first sulphonic group introduced into benzene ring facilitates introduction of the second sulphonic group into meta direction.



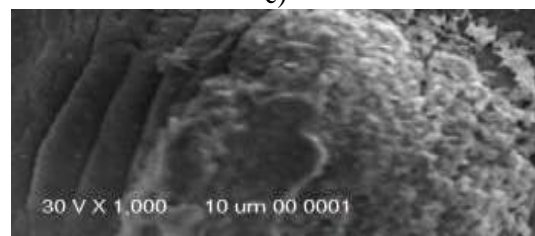
a)



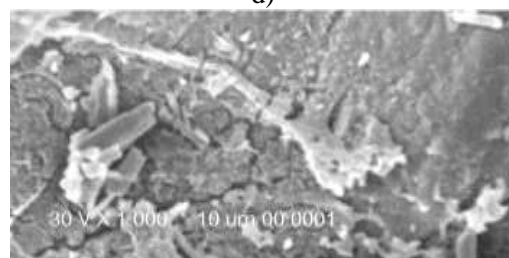
b)



c)



d)



e)

Fig. 6. Scan electron microscope of styrene and acrylic acid grafted onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes.

a) Pristine poly (tetrafluoroethylene).

b) 16% grafting yield.

c) 27% grafting yield.

d) 36% grafting yield.

e) 44% grafting yield.

TABLE 1. The grafted membranes characterization compared to Nafion 212.

No.	Membranes grafting yields (%)	Thickness (μm)	Water uptake (%)		Ion Exchange Capacity (mmol g^{-1})			Proton conductivity $\times 10^2$ (S/cm)			Tensile at break Strength (MPa)	Free volumes and gap (\AA)
			Amb. Temp.	80°C	Amb. Temp.	80°C	Further sulphonation at 80°C	Amb. Temp.	80°C	Further sulphonation at 80°C		
-1	16	51	4	7	0.22	0.28	0.476	0.27	0.38	0.615	71	9.035
-2	27	54	19	32	0.57	0.68	1.101	2.28	3.61	5.12	59	9.115
-3	36	59	32	43	0.77	0.89	1.380	4.76	5.66	7.68	51	9.184
-4	44	62	38	52	0.87	1.04	1.684	5.85	6.91	8.09	47	9.231
-5	Nafion-212	52	20	31	0.94	1.13	-----	6.31	7.13	-----	37	8.266

The porous membranes had strong ability to enhance H^+ and gasses diffusion, so on increasing the ion exchange capacity, water uptake and proton conductivity occurred.

By increasing the membranes' pore number and their volume (not exceed 10 nm), the fuel cell efficiency will be raised up. The membranes tensile strengths (47-71 MPa) of the membranes (at high IEC up to 1.09 mmol/g) were higher than Nafion 212 (37 MPa at IEC = 1.13 mmol /g). This was because the large pendent sulfonic group (SO_3)⁻² existed out of polymer chain plane (as it hanging upon styrene ring at the prepared membranes) can hinder molecular internal rotation and also enhanced intermolecular interaction⁽³⁰⁾. These data indicated membranes were strong to meet the mechanical property requirements for PEMFC applications.

Fuel cell performance

The fuel cell performance based highest grafting yield of styrene and acrylic acid onto poly (tetrafluoroethylene) possessed 0.5% alumina nanoparticles and Nafion 212 was performed. The understudied membrane performance compared to Nafion 212 at the fuel cell (at 80 °C and 100 % RH), was shown at Fig. 7 and 8. The membranes' function in a proton exchange fuel cell is to act as a gas barrier stopping the mixing of anode and cathode gases, and to facilitate H⁺ and water transport. The membranes' conductivities were crucial factor in fuel cell performance. Membrane water permeability was similarly a crucial key for optimized water transport between the electrodes⁽³¹⁾. The PEMFCs performance loss main source was believed to be due to water restricted mass transport to reaction sites^(32, 33). The cell performance behavior showed approximately linear relation at low current densities followed by curving towards limiting current indicating mass transport limitation behavior at high current densities. The fully humidified system (100 % RH) stream along with large amount of water produced at high current densities could lead to flooding if water was not removed quickly via the membrane (back diffusion). It can be seen that; the prepared membranes performance peak was at 0.64 W/cm² which was higher than Nafion 212 with 14%.

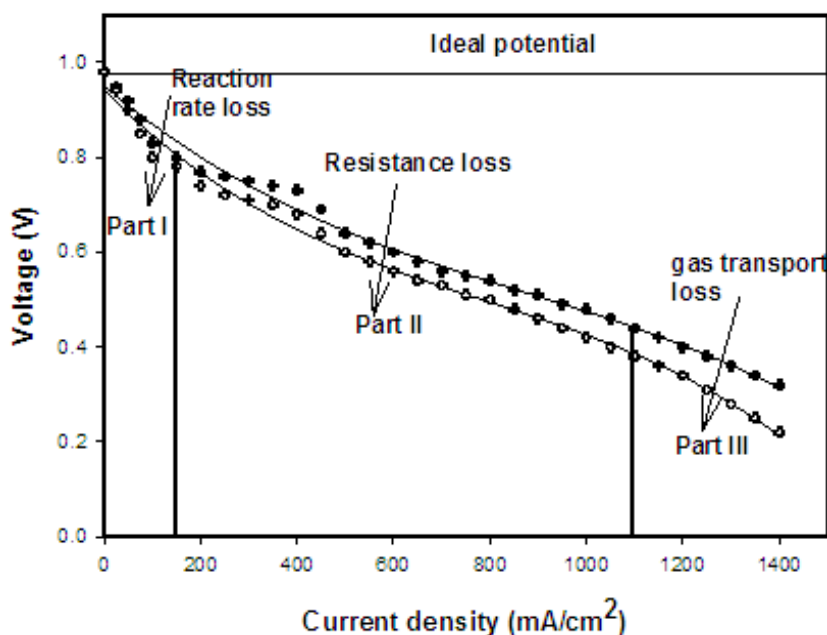


Fig. 7. Cell performance (current densities against voltage) of 44% grafting of styrene and acrylic acid onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes at 100% RH and 80 °C.

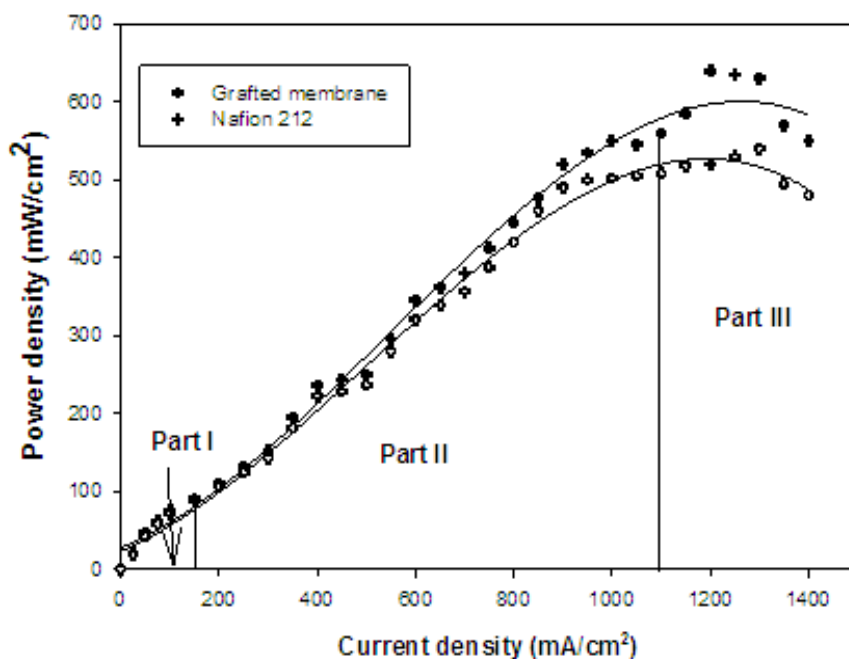


Fig. 8. Cell performance (current densities against power densities) for 44% grafting of styrene and acrylic acid onto poly (tetrafluoroethylene) with 0.5% nanoparticles alumina membranes at 100% RH and 80 °C.

Fuel cell durability

Further investigations will be conducted to assess the highest grafted yield membranes and furthermore sulphonation (PTFE possessed 0.5% alumina nanoparticles grafted with styrene and acrylic acid) durability. The Nafion-based cell voltage progressively decreased from 0.44 to 0.36 V up to 450 hr operation. It is showed in Fig. 9 the same behavior for the prepared membranes while their loss was to 0.39 V. This decrease in cell voltage was due to starting degradation of the understudied membranes, resulting in pinholes formation. It allowed the reactant crossover for the prepared membrane and Nafion 212 while the first is more durable than the latter⁽³⁴⁾. The continuous increasing crossover could also be verified by the decrease in open circuit voltage (OCV) 0.450 V. Furthermore, the Nafion 212 thickness in the active area decreased about 10% due to the membrane degradation⁽³⁵⁾ while the decrease in the prepared membranes thickness did not exceed 8%. Therefore, each of Nafion 212 and the prepared membranes were suitable for application in a fuel cell especially at the optimized condition.

TABLE 2. Classification of the fuel cell performance results .

No.	Comparative parameters	Part I	Part II	Part III
1	Range of voltage and power density results	0-150 mA/cm ²	150-1100 mA/cm ²	1400-1100 mA/cm ²
2	durability Range	75-0h.	275-75h.	450-275h.
3	Behavior of results	Overlapping results between grafted membranes and Nafion 212	Fragmentation results between grafted membranes and Nafion 212 with low extent	Fragmentation results between grafted membranes and Nafion 212 with large extent

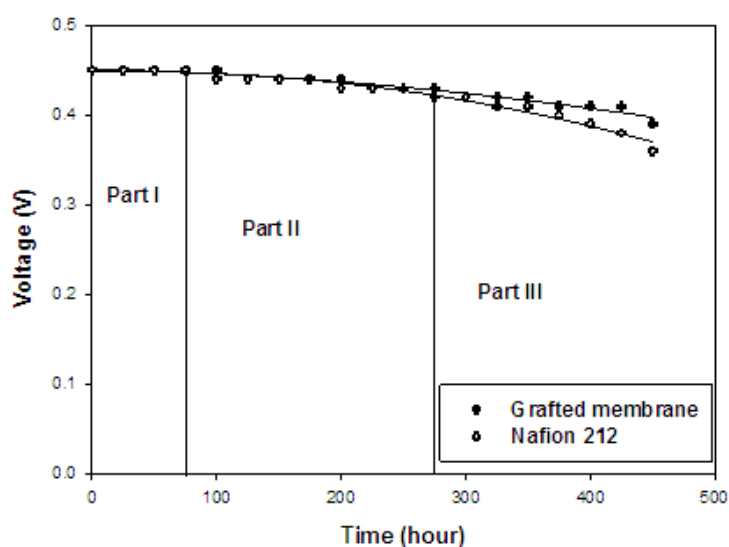


Fig. 9. Cell potential changes with time at fixed current density (600 mA/cm²) for 44% grafting of styrene and acrylic acid onto poly (tetrafluoroethylene) with 0.5 % nanoparticles alumina membranes and Nafion-212 at 80 °C and 100% RH.

Classification of the fuel cell performance results

Table 2 tabulated the comparison of Nafion 212 and the highest grafting yield (44%) of styrene and acrylic acid onto poly (tetrafluoroethylene) membranes (with 0.5 nanoparticles alumina) and furthermore it sulphonated in accordance to the fuel cell performance.

At the first part; performance results of both the grafted membranes and Nafion-212 have overlapped. At the second part; performance results of Nafion-212 and grafted membranes have fragmented. The grafted membrane performance and durability results exceed Nafion 212 with low extent. At the third part; performance and durability results of the grafted membrane is better than Nafion 212 with larger extent. These results conducted the ability of the prepared membranes to successfully replace the Nafion-212.

Conclusion

The goal of this work is; the preparation of low cost and compatible membranes with Nafion 212. Grafting of styrene and acrylic acid onto poly (tetrafluoroethylene) (with 0.5 % nanoparticles alumina) was done successfully using gamma irradiation as a facilitating tool. It was found that; 40 kGy gamma irradiation dose and 60% styrene: 40% acrylic acid were the optimum dose and monomers concentration ratio, respectively for achieving the highest grafting yield. Chemical and morphological structure investigations were performed using fourier transformer infra-red (FT-IR) spectroscopy and scan electron microscopy, respectively. Some impacts such as water uptake, ion exchange capacity, proton conductivity, free volumes size and tensile strength were studied to examine the membranes availability into the proton exchange membrane fuel cell (PEMFC). Fuel cell performance ensured that; the prepared membranes have capability to generate electricity and strongly compete with Nafion 212. The prepared membranes showed high durability up to 450 hr which recommend their utility into PEMFC.

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