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### **Polymer electrolyte membranes for fuel cells by radiation induced grafting with electron beam irradiation: state-of-the-art**

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#### **ABSTRACT**

SDS - PAGE was performed on desert locust, *Schistocerca gregaria* (Forsk.) fat body tissues of solitary form of the 5<sup>th</sup> nymph instar, three different phases of adult males and females namely; newly emerged, yellow and non-yellow males (mature and non-mature), before and after oviposition females of *Schistocerca gregaria*. The total number of protein bands detected in the fat body of the 5<sup>th</sup> nymph instar amounted to 25 bands, meanwhile, those detected in the fat body of newly emerged males, non-mature males and mature males were 22, 19, 21 respectively. On the other hand, the number of protein bands detected in the newly emerged females were 28 bands. These bands varied in the successive female phases to be 21 and 30 bands before oviposition and after oviposition respectively.

One protein band was detected in males only and considered as a male specific protein (MSP) whereas, four bands were detected in females only and considered as female specific proteins (FSP). Ten protein bands were considered as major fat body protein bands since they were commonly detected in all the investigated phases.

**Key Words:** *Protein variations, electrophoresis, fat body, solitary form, Schistocerca gregaria.*

#### **INTRODUCTION**

Polymer electrolyte membranes have generated considerable interest in various fields of industrial interest due to their wide spread applications in fuel cells, batteries, electrolyzers sensors and actuators. Such diversity in applications implies a strong demand to architect the membranes to attain particular properties for specific applications. Of all applications, fuel cell technology is one of the key technologies that are receiving tremendous efforts to bring about new environmentally friendly and highly efficient power source in the 21 century. Polymer electrolyte fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are the most promising fuel cell candidates for low temperature stationary and mobile applications operations. During normal PEMFC or DMFC operations, anodic dissociation of hydrogen in the former and methanol in the latter with Pt catalyst produces protons that are transported through the hydrated proton exchange membrane (PEM) to the cathode, where reduction of O<sub>2</sub> produces water<sup>(1)</sup>.

At present, the cost of these fuel cell systems is very high mainly due to the excessive cost incurred by some key components including PEM<sup>(2)</sup>. Several PEMs are commercially available

including Nafion<sup>TM</sup> (DuPont), Aciplex<sup>®</sup> (Asahi Chemicals Co.), Flemion<sup>®</sup> (Asahi Glass Co.), Gore-Tex (Gore and Associate), Ballard Advanced Materials (BAM), (Ballard) and Dais membranes, (Dais Co.). Of all, Nafion membrane is the most established product that has been widely tested and the majority of the available fuel cell systems are based on it. However, Nafion is expensive and has high methanol permeability (in DMFC). In addition, it is prone to viscoelastic relaxation at high temperatures (low hydrated  $T_g$ ), which decreases both its mechanical properties and proton conductivity<sup>(3)</sup>. This situation has triggered rather extensive worldwide efforts to develop alternative cost effective and highly conductive PCM membranes. Since then, varieties of alternative proton conducting membranes have been developed using various grafting techniques. The latest progress on these membranes and their different classes has been recently reviewed in several articles and book chapters<sup>(1,4-6)</sup>.

Radiation induced grafting of vinyl and acrylic monomers onto polymeric films, is an appealing method for producing various polymer electrolyte membranes. This method has the advantages of simplicity, controllability over the composition leading to tailored membrane properties and absence of shaping problem as preparation starts with substrate in a film form. It also has the flexibility of using various types of radiations such as  $\gamma$ -rays and electron beam. Of all, electron beam (EB) accelerator is an advantageous source of high energy radiation that can initiate grafting reactions required for preparation of the membranes particularly when pilot scale production and commercial applications are sought. The grafting penetration can be varied from surface to bulk of membranes depending on the acceleration energy<sup>(7)</sup>.

To obtain alternative fuel cell membranes using radiation induced grafting method, our research group developed two types of membranes for DMFC and PEMFC using simultaneous irradiation grafting with EB for first time and single-step method for grafting of sodium styrene sulfonate onto pre-irradiated fluorinated polymer films. The obtained membranes were found to possess an excellent combination of physical and chemical properties suitable for fuel cell application provided they have sufficient stability<sup>(8-16)</sup>. The objective this article is to review recent progress in the use of simultaneous and pre-irradiation graft copolymerization methods for preparation of proton exchange membranes for fuel cells using EB. Some basic fundamentals of radiation grafting are also briefly reviewed to highlight the significance of the latest development.

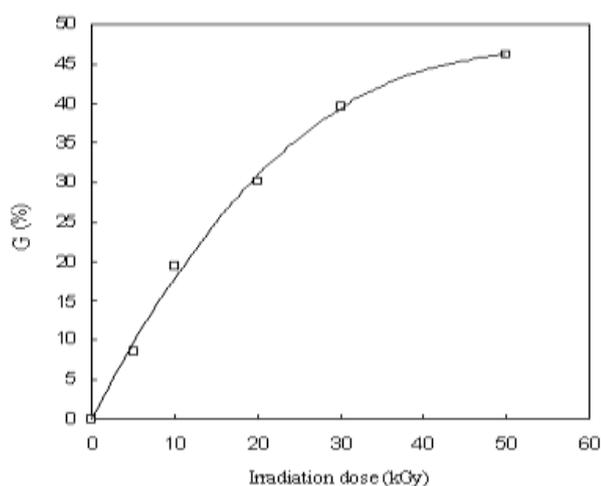
#### Radiation induced graft copolymerization

Radiation-induced graft copolymerization is a simple method for modification of existing polymers and imparting new properties without altering their inherent properties. Therefore, it had been of particular interest for preparation of a variety of functional membranes in past 5 decades. In this method active sites are formed on the polymer backbone using high energy radiation, which is subsequently allowed to react with monomer units and then propagate to form side chain grafts covalently bonded to the backbone of the polymer film when terminated. Two standard methods of radiation-induced graft copolymerization: i) direct (simultaneous) and ii) pre-irradiation methods have been developed over the past 50 years. In direct method, the base polymer is irradiated while immersed in the monomer solution forming free radicals in both polymer and monomer. Alternatively, in pre-irradiation, the base polymer is irradiated first (in inert atmosphere) to form trapped radicals and subsequently brought into contact with the monomer solution under controlled conditions. If irradiation step is carried out in air, the formed radicals react with oxygen forming peroxides and

hydroperoxides, which decompose at elevated temperature to initiate grafting reaction in presence of a monomer under controlled conditions and this method, is then called ‘peroxidation’. Each one of these grafting methods has its merits depending on polymer/monomer combination. For example, the direct method is very simple and efficient from polymer radiation chemistry principle viewpoint and produces higher degrees of grafting due to efficient utilization of radicals. On the other hand, pre-irradiation methods are very effective in reducing homopolymerization particularly upon grafting of highly reactive monomers such as acrylic acid and when pilot scale production is sought. Nonetheless, obtaining desired grafting levels in both grafting methods requires achieving optimum combinations of reaction parameters to vary the penetration depth of the monomer into the polymer bulk to eventually allow manipulation of the graft copolymer composition. The degree of grafting can be calculated by:  $G (\%) = 100 \times [(W_2 - W_1)/W_1]$ , where  $W_2$  and  $W_1$  are the weight of the film after and before grafting. A detail account for the advantages and disadvantages of both radiation-induced graft copolymerization methods can be found in Ref. 4

### Irradiation sources

Various types of high energy (ionizing) radiations sources in forms of either electromagnetic radiation, such as x-rays and gamma rays, or charged particles, such as heavy ions and electrons are available for grafting initiation irrespective of the shape and size of the polymer. Co-60 is the main source of gamma radiation, which has a half-life of 5.3 years and emits radiation of  $1.25 \pm 0.7$  MeV, and is frequently used to prepare functional membranes using both simultaneous and pre-irradiation methods. However, electron beam irradiation was found to be most effective in preparation of membranes using pre-irradiation method and when industrial usage is sought. This is because of its high irradiation dose rate, short processing time, ease of generation of free radicals in many polymers, moderate initiation reaction conditions and availability of wide range of commercial accelerators capable of producing energy in the range of 0.2-10 MeV <sup>(17)</sup>. Depending on the acceleration energy of electron beam and reaction parameters, it is possible to extend the modification of a polymer film to a specific depth ranging from the surface to the bulk of the polymer <sup>(7)</sup>.



**Fig. 1. Variation of the degree of grafting with the irradiation dose. Irradiation and grafting conditions are: accelerating voltage 0.5 MeV; beam current, 1.0 mA; dose per pass, 5 kGy; conveyor speed, 1.45 m/min; irradiation time 0.8-8 min; temperature, ambient; atmosphere, nitrogen; film thickness, 117.7  $\mu$ m and pure styrene.**

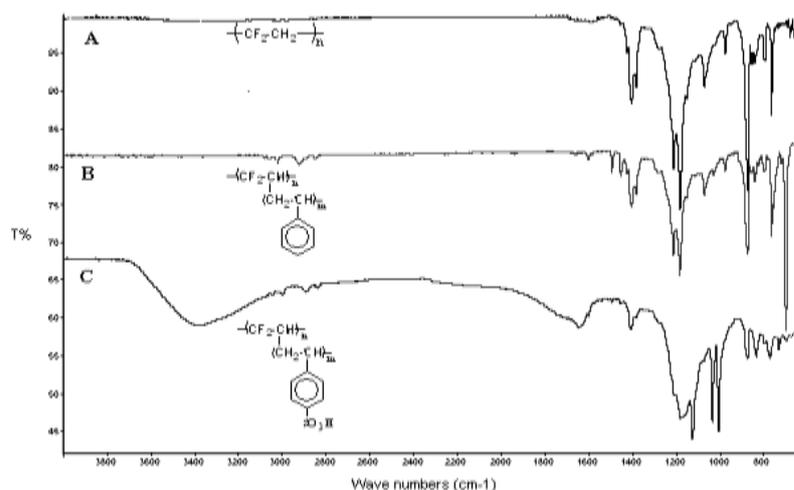
## PROTON CONDUCTING MEMBRANES USING SIMULTANEOUS IRRADIATION WITH ELECTRON BEAM

Recently, membranes prepared by radiation-induced grafting of styrene onto dense poly(vinylidene fluoride) PVDF films followed by sulfonation have driven growing interest after their superior performance was realized in DMFC<sup>(18)</sup>. These membranes were prepared by pre-irradiation method with electron beam (EB) based on combination of styrene and dense PVDF films followed by sulfonation<sup>(18)</sup>.

Earlier, Yamaguchi et al. have proposed pore-filled (composite) polyelectrolyte membranes as alternative membranes for the use in DMFC<sup>(19)</sup>. The proposed membranes were prepared by grafting a mixture of acrylic acid, sodium vinyl sulfonate and divinylbenzene into porous PTFE matrix using visible radiation and subsequent heat treatment followed by chemical treatment to obtain the acid form. The structural morphology of these membranes which has a combination of inert and mechanical stable porous substrate hosting highly conductive and swollen filling polyelectrolyte, allows tuning of their properties through controlling the fraction of polyelectrolyte and its swelling. Similar membranes have been also prepared using photochemically-induced grafting<sup>(20)</sup> and plasma-induced grafting<sup>(21)</sup>.

However, such membranes were dedicated to purification and separation applications because of limitations arising of surface and pore surface modification<sup>(9)</sup>. On the other hand, preparation of membranes having polystyrene sulfonic acid (PSSA) anchored in porous polymer matrix using high energy radiation has not exploited until recently when PSSA pore filled PVDF was reported by our group. In pursuing these membranes, a simultaneous irradiation method with EB was adopted to graft styrene impregnated in a porous PVDF film followed by sulfonation. The use of this method is believed to be useful in simplifying the membrane preparation process, reducing the monomer consumption and the homopolymer formation, along with a possible reduction of the overall cost of the membrane<sup>(9-11)</sup>.

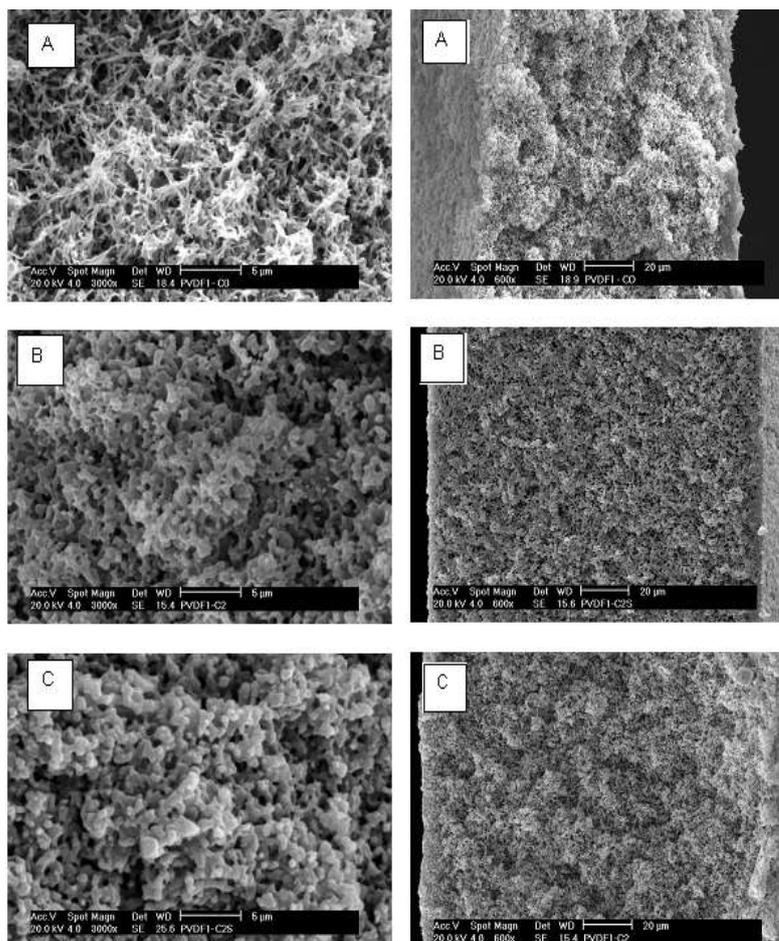
The membranes were prepared by loading styrene into PVDF porous matrix followed by irradiation with EB under selected reaction parameters. The obtained polystyrene (PS) pore-filled PVDF films were subsequently sulfonated under controlled conditions to confer the ionic character. The G% was found to increase steeply with the increase in the irradiation dose as shown in Fig. 1. G of 46% was achieved in the PVDF porous structure at an irradiation dose of 50 kGy under N<sub>2</sub> atmosphere and ambient temperature with a reduction in the porosity from 70 to 5% after porous PVDF was subjected to grafting and sulfonation.



**Fig. 2. Typical FTIR spectra of (A) pristine PVDF film (B) PS pore-filled PVDF film (G = 30%) and (C) its corresponding PSSA pore-filled PVDF membrane.**

### **Evidence of formation of polystyrene sulfonic acid in porous PVDF**

The incorporation of polystyrene sulfonic acid (PSSA) in the obtained membranes was verified using FTIR-ATR spectral analysis, as shown in Fig. 2. Grafting of styrene is confirmed by the presence of aromatic ring features established by the presence of skeletal C=C in plate-stretching vibrations at 1493 and 1602  $\text{cm}^{-1}$  together with C-H aromatic stretching vibrations at 3100-3026  $\text{cm}^{-1}$  together with a mono-substituted benzene ring peak at 749  $\text{cm}^{-1}$ . Sulfonation of PS pore-filled PVDF film is confirmed by the presence of the sharp peaks at 1126 and 1007  $\text{cm}^{-1}$ , which are due to the introduction  $\text{SO}_3^-$  groups. The peak at 1034  $\text{cm}^{-1}$  is assigned for the di-substituted benzene rings of PSSA. The broad peak at 3410  $\text{cm}^{-1}$  is assigned for -OH of water molecules involved in hydrogen bonding with  $\text{SO}_3^-$  groups.



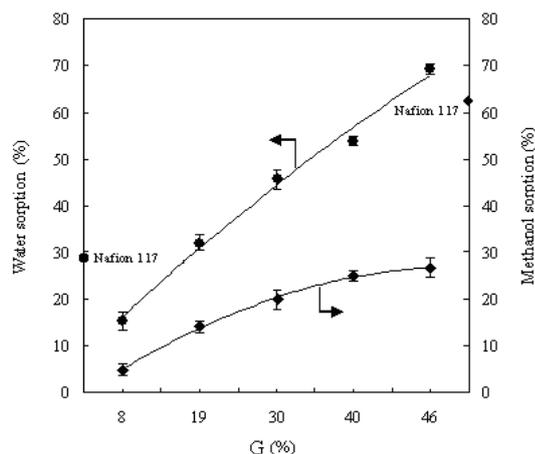
**Fig. 3.** SEM micrographs of the cross sections of: (A) pristine PVDF film, (B) PS pore-filled PVDF film with  $G = 30\%$  and (C) its corresponding PSSA pore-filled PVDF membrane (Higher and smaller magnifications).

### Morphology of the membranes

SEM micrographs of the cross sections of pristine PVDF film, 30% PS pore-filled PVDF film and its corresponding PSSA pore-filled membrane are shown in Fig. 3, respectively. As can be seen PS grafts overwhelmingly invaded the fibrous microstructure of PVDF film converting it into distinctive spherical particles with macroscopic phase separation. A small number of intersected pores remains scattered in the structure despite being thickened to great extent. Sulfonation of the membranes caused further reduction in the remaining pores and converted spherical particles into gel-like clusters (cationic domains) with bigger size. The structure of the sulfonated membranes appears uniform with no distinction between polystyrene sulfonic acid cluster domains and the PVDF matrix.

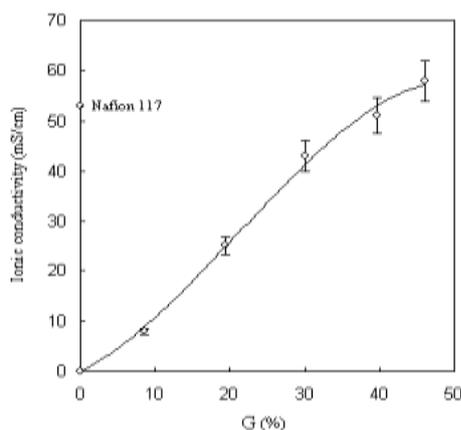
### Properties of the obtained pore-filled composite membranes

The physical and chemical properties including swelling, ion exchange capacity, the ionic conductivity and the methanol permeability of the membranes were evaluated with respect to degree of grafting ( $G\%$ ) i.e. the content of PS in the pores when sulfonation. Commercial Nafion 117 membrane was used for comparison. The obtained membrane achieved a degree of sulfonation close to 100 % i.e. the ratio of sulfonic acid groups to phenyl groups is approximately equal to 1.



**Fig. 4. Variation of water sorption and methanol sorption with the degree of grafting in PSSA pore-filled PVDF membranes. Nafion 117 is included for comparison.**

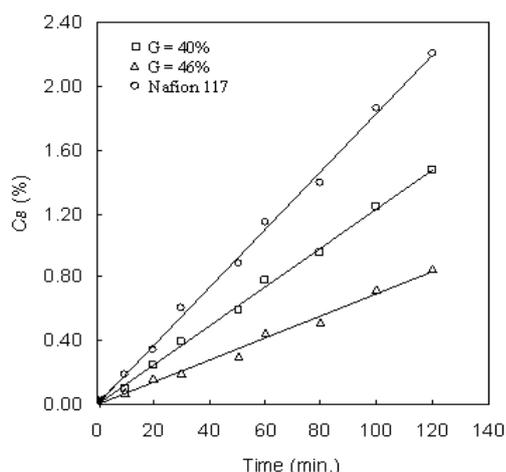
The swelling behavior of PSSA pore-filled PVDF membranes was found to be a function of G % as shown in Fig. 4. The increase in both water and methanol sorption with the increase in G% is attributed to the incorporation of more strongly hydrophilic sulfonic acid groups. On the other hand, the remarkable increase in the sorption of water at all grafting levels compared to that of methanol indicates that these membranes have preferential sorption for water over methanol. This was confirmed by the data of water/methanol ratio, which was found to be above unity ( $2.3 \pm 0.2$ ) although it does not practically vary with the increase in G%. Accordingly, it can be stated that PSSA pore-filled PVDF membranes have higher interactions towards water compared to methanol and both liquid sorption is limited to the hydrophilic PSSA domains in the membranes. Moreover, hosting of PSSA into the structure of PVDF has reduced the swelling from 98% for bulk PSSA <sup>(22)</sup> to 68% at G = 46% in the obtained membranes suggesting an effective suppression of the swelling by the porous hydrophobic substrate.



**Fig. 5. Variation of the ionic conductivity of the PSSA pore-filled PVDF membrane with the grafting yield. Nafion 117 is included for comparison.**

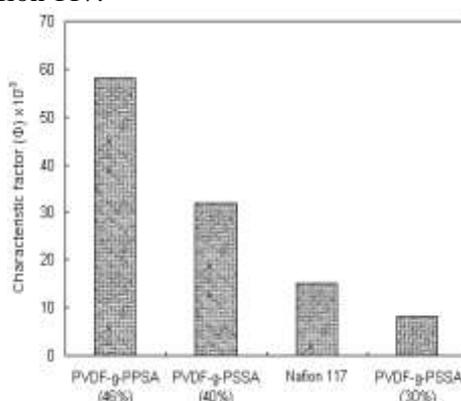
The dependence of the ionic (proton) conductivity of PSSA pore-filled PVDF membranes on G% presented in Fig. 5 is caused by the increase in both sulfonic acid groups associated with the pore-filling and the amount of sorbed water leading to better environment for the proton mobility in these

polymer electrolytes. 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 observed at  $G = 40$  and  $46\%$ , suggests that the water swollen ionic domains occluded in the membranes pores are most likely inter-connected forming a possible network structure. Therefore, the lower value of the ionic conductivity observed for membranes with low grafting yields such as  $8$  and  $19\%$  is due to the diffusion limitation caused by the segregation in the ionic domains. As  $G\%$  increases to sufficient level ( $30\%$ ), the ionic domains become more inter-connected and reach the percolation threshold beyond which the diffusion limitations are overcome allowing proton conductivity to reach its maximum value.



**Fig. 6.** Variation of the methanol concentration in the water compartment with time for PSSA pore-filled PVDF membranes having various degrees of grafting and Nafion 117 membrane.

The methanol permeability test was performed to evaluate the potential application of PSSA pore-filled PVDF membranes in DMFC after exhibiting higher water sorption selectively and equivalent ionic conductivity to Nafion 117 membrane and the obtained are presented in Fig. 6. The lower methanol permeability demonstrated by PSSA pore-filled PVDF membranes particularly at  $G = 40$  and  $46\%$  compared to Nafion 117 ( $53\%$  and  $71\%$  of that of Nafion 117, respectively) indicates that a significant reduction in methanol cross-over could be achieved using the membranes developed in this work. This can be mainly ascribed to the lower methanol sorption in PSSA pore-filled PVDF membranes compared to that of Nafion 117.



**Fig. 7.** Comparison of the characteristic performance evaluation factor of PSSA pore-filled PVDF membranes with various grafting yields ( $30$ ,  $40$  and  $46\%$ ) and Nafion 117 membrane.

The overall performance of each membrane including Nafion 117 was evaluated in terms the performance evaluation factor ( $\Phi$ ) which is the ratio of the ionic conductivity to the methanol permeability for three selected ( $G\% = 30, 40$  and  $46\%$ ) PSSA pore-filled PVDF membranes compared to Nafion 117 membrane as presented in Fig. 7. The PSSA pore-filled PVDF membranes having  $G$  of  $40$  and  $46\%$  were found to respectively recorded  $\Phi$  ( $32$  and  $58$ ) higher than that of Nafion 117 ( $\Phi = 15$ ) by two and three folds suggesting that these membranes are suitable for application in DMFC. Such decrease in the methanol permeability in the presence of high ionic conductivity was found to improve the cell efficiency and the power density.

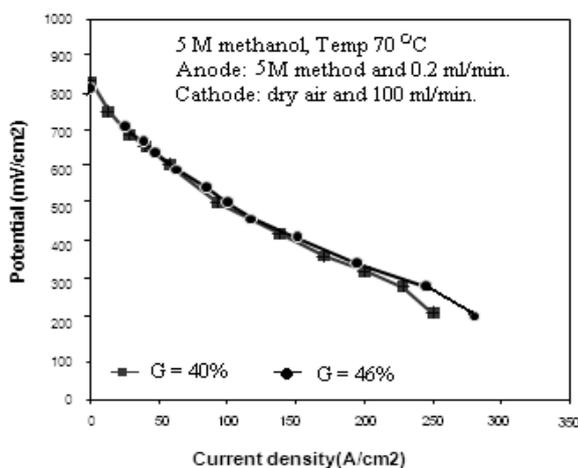


Fig. 7. Cell voltage-current density relations of the single DMFC cell using PSSA pore-filled PVDF membranes.

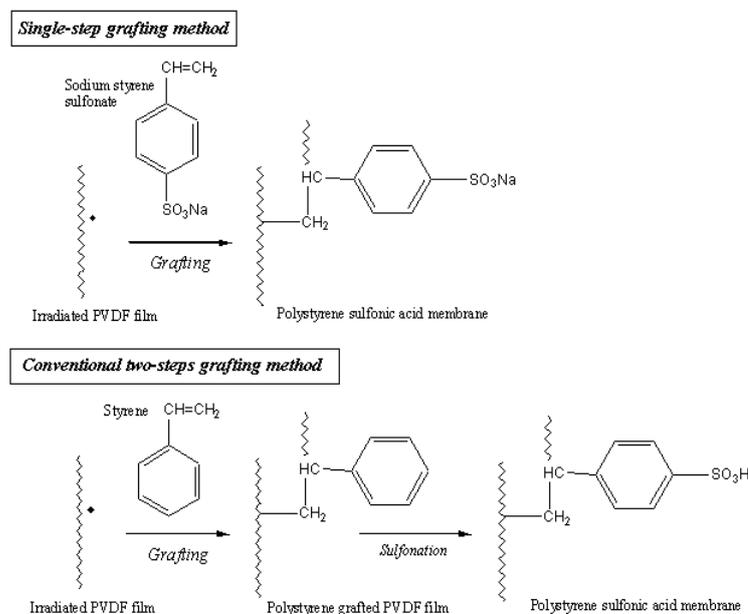
### Testing the performance in DMFC

The PSSA pore-filled membrane was assembled with standard electrodes and tested in DMFC until fuel cell failure. Fig. 8 shows polarization curves for a single DMFC with grafted membranes. An open circuit voltage of  $820$  and  $830$  mV was observed for  $40$  and  $45\%$  grafted membranes, respectively at a constant temperature of  $70^\circ\text{C}$ . The performance of the single cell with  $G = 45\%$  is slightly better than that of  $G = 40\%$  and this can be attributed to higher conductivity and lower methanol selectivity in the former than the latter. Since these membranes have less preference to methanol permeation i.e. less fuel crossover, an efficiency performance of DMFC can be anticipated. The test duration varied from  $180$  to  $200$  h, which was found to vary depending  $G\%$ . The failure was marked by a sudden drop in OCV that was found to be caused by delamination of the membranes, which becomes brittle.

### PROTON CONDUCTING MEMBRANES BY RADIATION INDUCED GRAFTING OF SULFONATED MONOMER

Radiation grafted membranes have been found to be potential alternatives for commercial fuel membranes. Radiation grafted proton conducting membranes are commonly prepared by grafting of styrene, styrene/crosslinker mixtures, or substituted styrene monomer onto fluorinated polymer films followed by a sulfonation reaction to confer the polystyrene grafted films pendent ionic characters<sup>(4-6)</sup>.

Sulfonation is commonly performed using a strong sulfonating agents such as chlorosulfonic acid diluted with chemical-resisting solvents (e.g. 1,2-dichloromethane) under controlled parameters. However, achieving a degree of sulfonation of 100% i.e. every benzene ring only contains one pendant sulfonic acid group without compromising the mechanical strength of the obtained membranes together with the hazardous nature of sulfonation reaction pose a challenge that can be overcome by grafting a monomer already containing sulfonic acid such as sodium styrene sulfonate (SSS).



**Fig. 9. Schematic representation of preparation of proton exchange membrane in a single step reaction compared to conventional two-steps grafting method.**

Recently, few research groups have reported radiation grafting of SSS onto a limited number of polymer substrates including high density polyethylene (HDPE), polypropylene (PP) and poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) apparently for separation applications<sup>(23-30)</sup>. Because of poor SSS grafting kinetics caused by the incompatibility between the highly ionized hydrophilic sulfonic acid groups and the hydrophobic polymer backbone forcing very low grafting levels, acrylic acid (a co-monomer) is grafted prior to- or with SSS to promote grafting reaction<sup>(23-29)</sup>. Grafting of SSS without acrylic acid onto aromatic polyamides (nylon) under controlled conditions was also lately attempted by Li et al<sup>(30)</sup>. However, radiation induced grafting of SSS onto fluorinated films such as PVDF without addition of a co-monomer of acrylic acid has not been reported in literature until it was recently investigated by our groups .

**Table 1.** The effect of various solvents on the degree of grafting of SSS onto pre-irradiated PVDF film. Reaction conditions: Irradiation dose, 100 kGy; monomer concentration, 1 mol/L; reaction time, 24 h and temperature, 60°C.

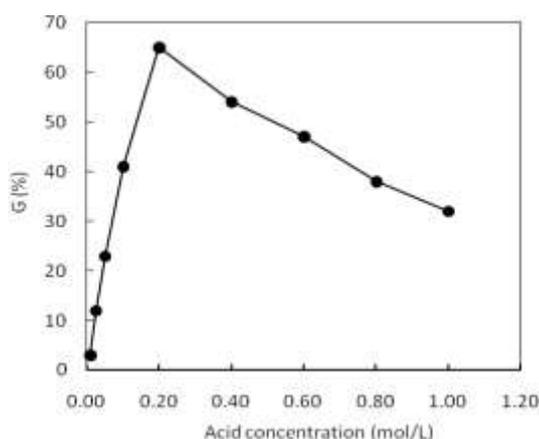
Solvents	<i>G</i> (%)
Water	0.0
Methanol	0.2
DMF	0.4
DMF/H <sub>2</sub> SO <sub>4</sub> (aq. solution) <sup>a</sup> (9:1 v/v)	65.

<sup>a</sup>acid concentration is 0.2M

### Proton conducting membranes by a single-step grafting method

A single-step method for the preparation of sulfonic acid proton conduction membranes by radiation induced grafting of SSS monomer onto PVDF films using the pre-irradiation method for a possible use in PEMFC has been investigated <sup>(14)</sup>. Figs. 9 shows a schematic representation of preparation of proton exchange membrane in a single step reaction compared to conventional two-steps grafting method.

In this method, SSS having concentration 1.0 mol/L diluted with a mixture of DMF and sulfuric acid solution (0.2 mol/L) was grafted onto PVDF films irradiation up to a total dose of 100 kGy. A degree of grafting of 65% was achieved compared to 0.4% without acid addition as shown in Table 1. Such degree of grafting matches the requirement for fuel cell and suggests that the acid addition was very essential for the grafting to embark from negligible levels to values suitable for fuel cell application for SSS/PVDF grafting system.



**Fig. 10.** Variation of the degree of grafting of SSS onto PVDF film with the acid concentration at a 10 vol% of total grafting solution volume. Reaction conditions: irradiation dose, 100 kGy; solvent, DMF; reaction time, 24 h, atmosphere, N<sub>2</sub> and temperature, 60°C.

### Synergetic effect of acid addition

Fig. 10 show the effect of variation of sulfuric acid concentration on the degree of grafting of SSS diluted with DMF onto PVDF film. The H<sub>2</sub>SO<sub>4</sub> acid concentration in the aqueous solution was varied in the range of 0.01-1.0 mol/L. *G*% was found to increase dramatically with increasing acid concentration until it achieved a maxima at a 0.2 mol/L beyond which it was sharply dropped with more acid content. This trend is presumably due to the increase in acid reactivity readily synergizes the monomer grafting to certain concentration extent (0.2 mol/L) beyond which grafting becomes lesser under the influence of rising viscosity of grafting solution that lowers the monomer diffusion and consequently propagating chains partly terminates by recombination.

The synergetic acid effect was attributed to the cumulative effect of the increase in the monomer supply to the graft growing chains under the influence of partitioning effect (partitioning coefficient of SSS between the PVDF film and the external liquid phase is modified by presence of acid in a way leading to an increase in swelling equilibrium and the local SSS concentration around the grafting sites), the inhibition of termination by recombination in the graft propagating chains and the suppression of homopolyme by Na-salt formed in the grafting solution. The role of acid in boosting the degree of grafting followed the sequence: H<sub>2</sub>SO<sub>4</sub>>HCl>CH<sub>3</sub>COOH>HNO<sub>3</sub><sup>(16)</sup>.

### Kinetic behavior for grafting of SSS onto EB-irradiated PVDF films

Investigation of the kinetics investigations of graft copolymerization of SSS onto EB irradiated PVDF films under various reaction conditions showed that the degree of grafting was found to be dependent upon the reaction conditions i.e. such as monomer concentration (0.2-1.0 mol/L), irradiation dose (20-100 kGy), reaction temperature (30-60°C), film thickness (50-80, and 120 μm) and storage time. Various degrees of grafting in the range of 5-65% were obtained with graft copolymerization essentially depends not only on the concentration of the monomer in the grafting sites but also on the amount of the activated radicals in the base polymer.

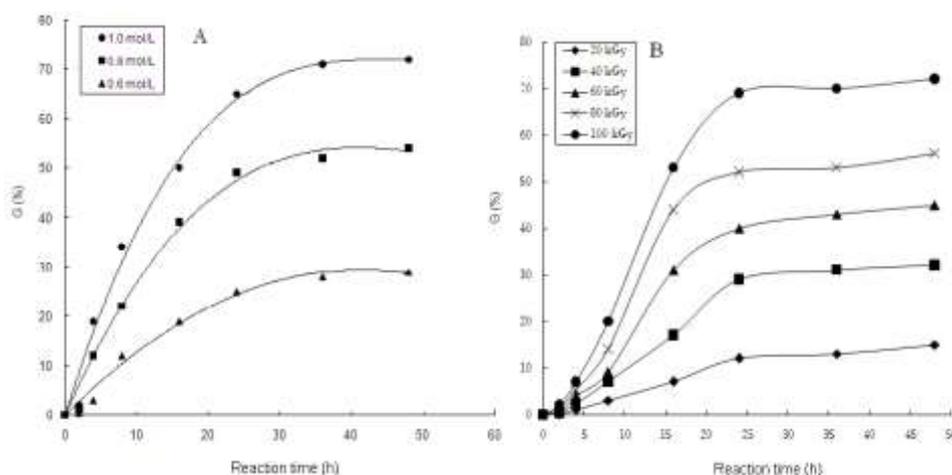
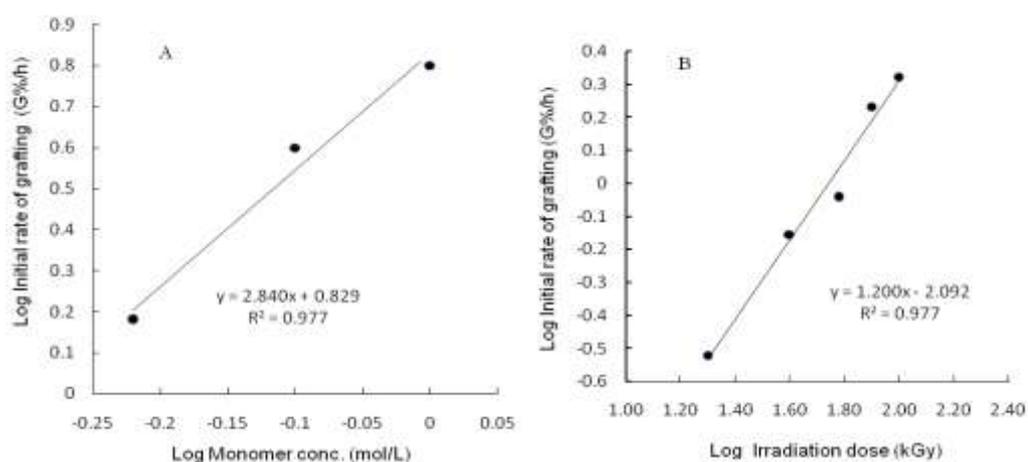


Fig. 11. Degree of grafting-time courses at: A) various monomer concentrations and B) irradiation doses for grafting of SSS onto PVDF film. Grafting conditions are: irradiation dose, 100 kGy; solvent, DMF; acid additive, 10 vol% of grafting solution at constant H<sub>2</sub>SO<sub>4</sub> concentration of 0.2 mol/L; temperature, 60°C; film thickness, 50 μm; and atmosphere, N<sub>2</sub>.



**Fig. 12. Log-log plot for initial rate of grafting versus: A) monomer concentration and B) irradiation dose for grafting SSS onto PVDF film. The data were obtained from Fig. 11.**

The degree of grafting-time courses at various monomer concentration and irradiation dose can be shown in Fig. 11.  $G\%$  was found to increase drastically with time increase at all monomer concentrations or irradiation doses for the first 24 h beyond which, it tends to level off.  $G\%$  was also found to increase drastically with the increase in the reaction time at all doses and tends to level off after 24 h. Moreover, the degree of grafting increases with the increase in the monomer concentration or dose at a particular time. The drastic increase in  $G\%$  can be ascribed to the acceleration in the monomer diffusion into polymer substrate containing activated radicals facilitated by the acid addition allowing propagation to continue for 24 h, on basis of the fact that higher monomer concentrations or higher doses lead to higher degrees of grafting. As the time increases, rapid decay in trapped radicals and chain mobility increase causing frequent bimolecular termination in the propagated graft chains most likely take place under the influence of prolonged heating leading to a slowdown in the rate of grafting.

The orders of dependence of initial rate of grafting on monomer concentration and irradiation dose were found to be  $2.84 \pm 0.63$  and  $1.20 \pm 0.2$ , respectively as obtained from Fig. 12. The value of the order of monomer concentration obtained for the present grafting system is not consistent with the first order dependence of classical free radical polymerization. Such higher order value can be explained on the basis of fast termination of growing chains by transfer to impurities, solvent and other constituents in the reaction medium. On the other hand, it can be obviously seen that the dose exponent of 1.2 is higher than the theoretical value of free radical polymerization, which equals 0.5 where high energy radiation plays the role of the initiator and the absorbed dose is considered equivalent to the initiator concentration. Such high dependency order on the absorbed dose reflects a possible decay, mutual recombination or partial consumption of some of the trapped radicals in partial crosslinking mostly took place in the PVDF matrix upon irradiation and formation of a denser polymer matrix<sup>(32)</sup>. This trend can be also attributed to the 'mechano-chemical' grafting effect suggested by Bozzi and Chapiro<sup>(33)</sup> similar high dependency on the dose dependence of grafting of styrene onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP).

The overall activation energy for graft copolymerization was calculated to be 11.36 kJ/mol. This value equals almost half of that reported for grafting of SSS and acrylic acid onto high density

polyethylene (HDPE) at a temperature range of 40-70°C (22.2 kJ/mol) but remains within the range commonly obtained for radiation induced graft copolymerization reactions (8-32 kJ/mol) when only considering the activation energy of propagation reaction i.e. neglecting initiation and termination activation energies<sup>(27)</sup>.

The initial rate of grafting and the final degree of grafting were found to be inversely proportional to the film thickness. The storage of irradiated films under -60°C up to 180 days does not cause major change in the grafting yield promoting the use of this method for practical preparation of membranes<sup>(31)</sup>.

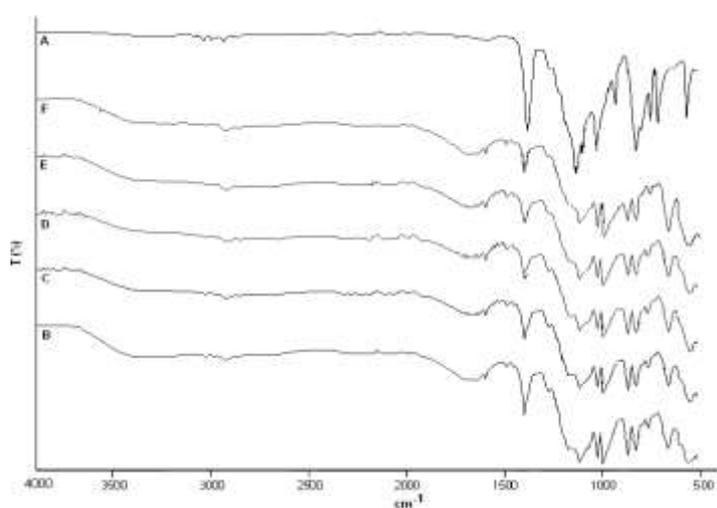


Fig. 13. FTIR spectra of: A) original PVDF film and PSSA grafted PVDF membranes with various degrees of grafting, B) 12%; C) 29%; D) 44%; E) 53% and F) 65%.

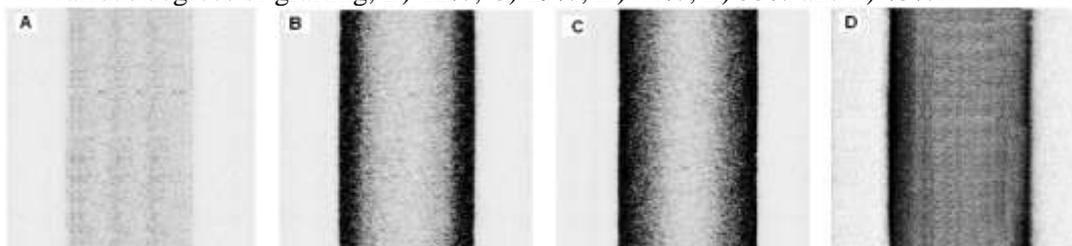


Fig. 14. Scanning optical microscopy images of cross-sections of A) original PVDF and dyed PSSA grafted PVDF membranes with various degrees of grafting, B) 12%, C) 29% and D) 53%.

### Evidence of grafting

Fig. 13 shows typical FTIR spectra of original PVDF film and grafted polystyrene sulfonic acid membranes having various degrees of grafting in frequency range of 500-2000  $\text{cm}^{-1}$ . Compared to original PVDF film, the grafted membranes displayed features confirming the presence of aromatic ring features established by the presence of skeletal C=C in plate-stretching vibrations at 1603 and 1495  $\text{cm}^{-1}$  together with in-plane CH notable band of bending vibration of the substituted benzene ring at 695  $\text{cm}^{-1}$ . The band at 1034  $\text{cm}^{-1}$  is due to the in-plane CH bending vibration of the di-substituted benzene ring. The bands at 1453, 1128, 1062 and 1000  $\text{cm}^{-1}$  are due to the presence of  $-\text{SO}_3\text{H}$  groups.

The intensity of the characteristics bands vary with the variation of the degree of grafting. From FTIR results, it can be confirmed that SSS was grafted onto PVDF films and PSSA membranes were successfully obtained.

### Graft distribution

Fig. 14 shows optical microscopy images of cross-section of dyed membranes having various degrees of grafting in comparison with original PVDF films. As can be seen the dyed part representing concentration of grafted ionic groups in the membrane was close to both surfaces at  $G = 12\%$  and increased with the increase in  $G$  to  $29\%$  until it covered the whole sample transverse plane at  $G = 53\%$  achieving a homogenous graft distribution. These observations indicate that grafting of polystyrene sulfonate started at layers close the surfaces of PVDF film and moved inward until both grafting fronts met achieving a homogenous distribution. These results provide evident that grafting the present system proceeded by front mechanism.

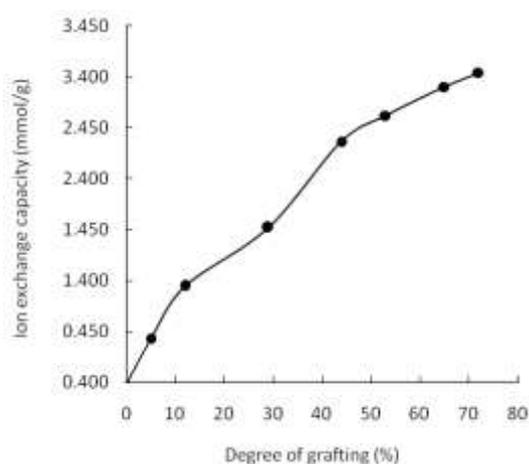


Fig. 15. The ion exchange capacity versus the degree of grafting of PSSA grafted PVDF membranes.

### Properties of proton exchange membranes obtained by single-step method

Fig. 15 shows the relationship between the degree of grafting and the ion exchange capacity of the membranes. The IEC increases with the increase in  $G\%$ . This can be attributed to the increase in the amount of sulfonic acid groups originated from the grafted SSS introduced to PVDF film. Since these membranes have a 100% degree of sulfonation, it is reasonable to relate all the membrane properties to IEC.

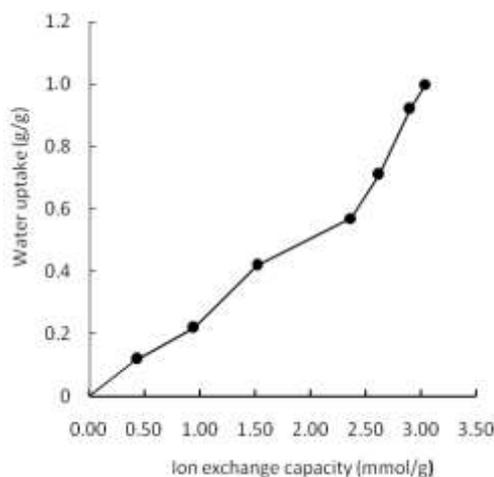


Fig. 16. The water uptake versus the ion exchange capacity of PVDF-g-PSSA membranes.

Fig. 16 shows the relationship between the water uptake and the ion exchange capacity of the membranes. As can be seen, the water uptake increases steeply with the increase in IEC. This is due to the increase in the number of hydrophilic sulfonic acid groups incorporated in the membranes. Since the obtained values of IEC represent degrees of sulfonation of 100% regardless of  $G\%$  in the membranes, the new method is advantageous compared to conventional one in which achieving complete sulfonation in polystyrene grafted films is difficult and compromises the resulting membranes physical strength.

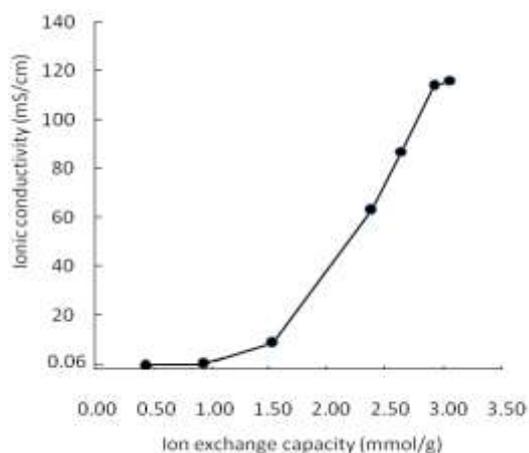


Fig. 17. The ionic conductivity versus the ion exchange capacity of PSSA grafted PVDF membranes.

Fig. 17 shows the relationship between the ionic conductivity and the ion exchange capacity of the membranes. As can be seen, the ionic conductivity increases slightly as IEC increases in the range corresponding to  $G$  of 5-30% then achieves a percolation threshold in the range of  $G$  of 30-65%. Further increase in IEC does not bring any significant change to the conductivity. Since, ionic conductivity is a function of IEC, water uptake and the distribution of sulfonic acid groups, the early slight increase in the conductivity was caused by the presence of sulfonic acid groups close to the surfaces of the membrane leaving the ungrafted bulk to resist the proton mobility. As the distribution

of sulfonic acid groups move rapidly towards the bulk of the membranes ( $G > 30\%$ ), a great increase in the conductivity occurred due to the gradual diminishing of proton transfer-resistant zones that was followed by achieving a homogenous distribution (at  $G = 65\%$ ) beyond which no considerable conductivity change could be observed. It can be suggested that, the incorporation of sufficient sulfonic acid groups with homogenous distribution provides better environment for the ionic mobility in the membranes. However, other structural properties such as the degree of crystallinity ( $X_c$ ) may have contributed to the increase in the conductivity as reported for similar polystyrene sulfonic acid membranes based on FEP<sup>(34)</sup>. A summary of the properties of some important membranes is given in Table 2. As can be seen the obtained membranes have a very good combination of physico-chemical properties suitable for PEMFC application.

Table 2. Summary of the physico-chemical properties of some of the membranes obtained by a single-step grafting method.

Degree of grafting (%)	Thickness ( $\mu\text{m}$ )	Water uptake (g/g)	H <sub>2</sub> O/SO <sub>3</sub> <sup>-</sup>	IE C (mmol/g)	Proton conductivity (mScm <sup>-1</sup> )
44	5 6	57	1 3	2.3 0	63
53	5 8	71	1 7	2.6 3	87
65	6 1	92	1 8	2.9 0	114

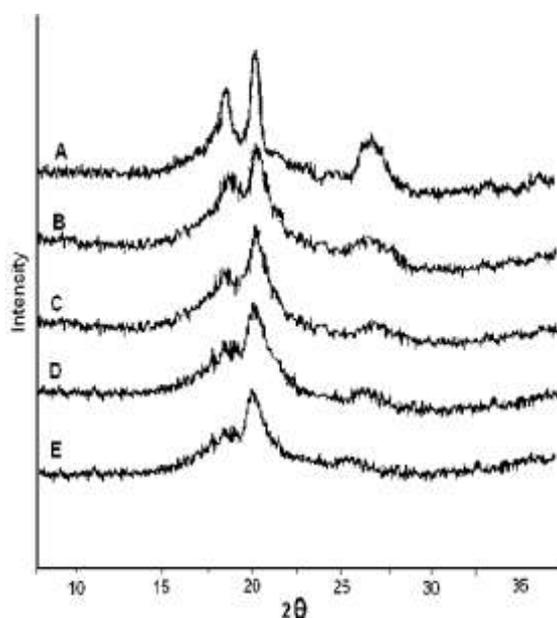


Fig. 18. XRD diffraction curves of: A) original PVDF film and PSSA grafted PVDF membranes with various degrees of grafting, B) 12%; C) 29%; D) 44%; E) 53% and F) 65%.

The structural changes caused by grafting of SSS onto PVDF films at various levels were investigated by XRD analysis and the obtained curves are presented in Fig. 18. Original PVDF film displays a typical diffraction curves that reflects the semi-crystalline nature of the polymer which have two crystal sizes. When grafted with SSS, the overall crystalline peaks area decreased and such decrease is a function of  $G\%$ . Coincidentally, there is no obvious shift in crystalline peak position appeared at Bragg's angle of  $2\theta = 19$  and  $21$ , respectively. These observations suggest a reduction in the inherent crystallinity of PVDF film is most likely caused by the dilution effect stemmed from the incorporation of amorphous poly(styrene sulfonic acid), which increases with the rise in  $G\%$ . It can be assumed that the semi-crystalline nature of PVDF is still preserved and grafting occurs in amorphous region of polymer matrix without causing disruption in crystalline structure. These results go along with crystallinity investigation conducted on these membranes with various  $G\%$  with DSC. Table 3 presents a summary of data obtained from DSC thermal analysis.

Table 3. Summary of data obtained from DSC thermal analysis.

Samples	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$	$X_c$
Original PVDF film	167.9*	139.9	39.2
PSSA-g-PVDF (16%)	166.4*	138.8	30.5
PSSA-g-PVDF (44%)	162.7	137.7	28.6
PSSA-g-PVDF (53%)	160.4	136.6	26.8
PSSA-g-PVDF (65%)	158.8	135.7	24.5

\*Refers to the main melting peak

The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ) of the membranes was found to decrease with the increase in  $G\%$ . The degree of crystallinity ( $X_c$ ) calculated from the area under the melting peak was also decreased with the increase of  $G\%$  PSSA content. This behavior suggests that the structural changes taking place in these membranes are solely caused by the dilution of the inherent crystallites of PVDF by the incorporated amorphous PSSA. Similar reduction in  $T_m$  and  $X_c$  was reported obtained by grafting of styrene onto PVDF film followed by sulfonation. However, such structural changes were attributed to a cumulative effect of dilution of the inherent crystallinity and partial disruption in the polymer crystalline structure <sup>(12)</sup>.

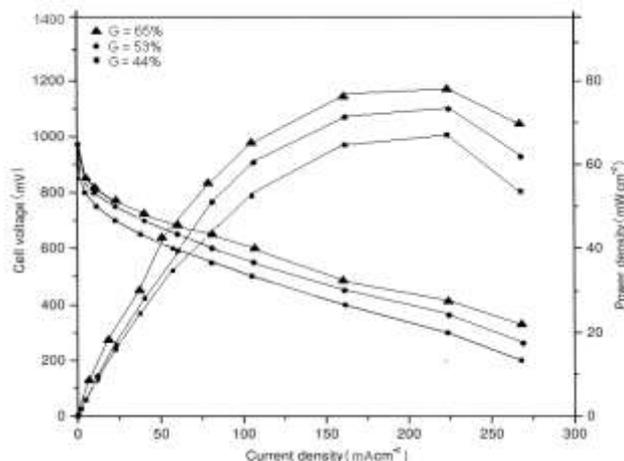


Fig.19. Current-voltage characteristics of PEMFC with polystyrene sulfonic grafted PVDF membrane having various  $G\%$ .

### PEMFC performance

PEMFC test was carried out at  $60^{\circ}\text{C}$  with three membrane-electrode-assemblies (MEAs) made of commercial electrodes and grafted membranes having  $G\%$  of 44, 53 and 65, respectively. Fig. 19 shows current-voltage characteristics of MEAs with PSSA grafted PVDF membranes. The current-voltage characteristics of the three MEAs have a similar trend with a maximum power density in range of  $67\text{--}78\text{ mW/cm}^2$  can be observed with variation of  $G$  in the range of 44–65%. This indicates that increasing  $G\%$  improves the polarization characteristics of the membranes and such behavior may be attributed to the higher proton conductivity and water uptake at high  $G\%$  values, both of which reduce the membrane resistance to proton transfer. The high open circuit values in all membranes ( $982 \pm 3\text{ mV}$ ) indicate that the tested membranes are gas tight and  $\text{H}_2$  or  $\text{O}_2$  permeation is independent of the thickness.

### CONCLUDING REMARKS

Two types of PSA grafted PVDF membranes were prepared using radiation induced grafting methods by means of EB. The first type of membranes is a PSSA pore-filled (composite) membrane was prepared using simultaneous EB irradiation grafting method where styrene was impregnated into porous the structure of PVDF films and the obtained precursor (polystyrene grafted films) was sulfonated. The use of this method not only simplified the pore-filling process and shortened the reaction time but also reduced the monomer consumption to a great extent. The membranes having  $G$  of 40 and 46% demonstrated higher ionic conductivity and lower methanol permeability than Nafion 117 membrane. The performance of PSSA pore-filled PVDF membranes developed in this work was found to be very promising for DMFC application.

The second type of membranes is a dense PSSA membrane prepared by a single step-grafting method involves grafting of sodium styrene sulfonate onto EB irradiation PVDF film in an acidic medium. This method provides a shorter and environmentally friendly route to prepare sulfonic acid membranes with the merit of elimination of the hazardous sulfonation reaction which render the whole process cost effective. The properties of the membranes were found to be dependent on  $G\%$ , which can be varied by manipulation of the parameters of the grafting reaction. The obtained membranes

showed an interesting combination of properties and a promising performance in PEMFC. Finally, it can be concluded that EB provides an effective irradiation tool to improve the economy of radiation induced grafting towards development of commercial products through shortening processing time, reducing monomer consumption and setting basis for continuous large scale facilities to produce radiation grafted sulfonic membranes.

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