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PREPARATION AND CHARACTERIZATION OF POLY(1-VINYL IMIDAZOLE)-*GRAFT*-ETFE/PHOSPHORIC ACID PROTON CONDUCTING MEMBRANES

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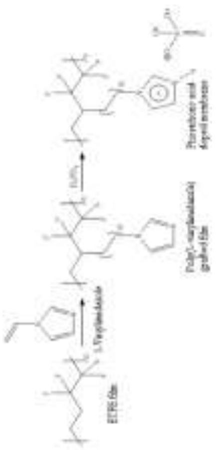
Graphical abstract



Abstract

Proton conducting membranes obtained by radiation-induced grafting (RIG) of 1-vinylimidazole (1-VIm) onto poly(ethylene-co-tetraflouroethene) (ETFE) films followed by phosphoric acid (PA) doping was prepared. The effect of grafting parameters on the grafted basic moiety was studied. The level of PA doping was controlled by manipulation of reaction parameters. The obtained membranes were investigated with Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), differential scanning calorimeter (DSC) and *DC* impedance spectroscopy. The obtained membranes proved to have less-water dependent proton conductivity with a value of 140 mS/cm at 120°C and 17 % RH% at acid doping level of of 6.54 mmol/repeat unit. The membranes have potential for application in high temperature polymer electrolyte membrane fuel cell (PEMFC).

Keywords: Radiation induced grafting; vinyl imidazole; ETFE film; phosphoric acid doping; composite membrane; high temperature PEMFC.

Abstrak

Membran konduksi proton telah diperolehi melalui cantuman disebabkan oleh radiasi 1-vinil imidazole (1-VIm) ke filem 'poly (ethylene-co-tetrafluoroethene)' (ETFE) diikuti dengan pencelupan asid fosforik (PA) telah disediakan. Kesan parameter cantuman pada bahagian cantuman basik telah dikaji. Tahap pencelupan asid fosforik telah dikawal dengan memanipulasi parameter tindak balas. Membran yang telah diperolehi telah dianalisis melalui 'Fourier transform infrared spectroscopy' (FTIR), 'thermal gravimetric analysis' (TGA), differential scanning calorimeter' (DSC) dan '*DC* impedance spectroscopy'. Membran yang diperolehi telah terbukti mempunyai kekonduksian proton yang kurang bergantung kepada air dengan nilai kekonduksian 140 Ms/cm pada suhu 120°C dan 17% kelembapan relatif pada tahap pencelupan 6.54 mmol/unit berulang. Membran tersebut mempunyai potensi untuk beroperasi dalam polimer elektrolit membrane sel bahan api (PEMFC) pada suhu tinggi.

Kata kunci: Radiasi disebabkan cantuman; vinil imidazole; filem ETFE; pencelupan asid fosforik; membran komposit; PEMFC suhu tinggi

1.0 INTRODUCTION

Fuel cells are one of fast growing alternative environmentally friendly power sources for meeting the fast growing energy demands in various sectors. Particularly, fuel cells utilizing proton exchange membranes as electrolytes are highly attractive for a variety of low temperature (60-80°C) applications. However, the potential use of PEMFCs is often limited by the poisoning effect caused by traces of CO in the reformed fuel. Moreover, commercial perfluorosulfonic membranes such as Nafion conduct protons by a water-dependent mechanism and therefore a water humidification system is installed to prevent the membrane drying and over wetting, leading an adverse increase PEMFC overall cost and system complexity.[1]

High temperature polymer electrolyte membrane fuel cell (HT-PEMFC) has been proposed for replacing PEMFC operating at low temperature. This is harness the benefits of high temperature operation including improvement of electrode kinetics, reduction/elimination of humidification, increment of tolerance to fuel impurities, enhancement of ionic conductivities and increment of values of excess heat by cogeneration.[2]

Currently, Nafion and its analogous membranes are deemed to be unsuitable in HT-PEMFC due to deterioration of their proton conductivity and gas retention properties. The former is based on proton flow in the aqueous phase of the membrane, which is hindered by dryness whereas the latter is caused by the variation in the membrane viscoelastic properties.[3] Therefore, the search for alternative proton conducting membranes that can sustain high temperature operation in PEMFC is fast growing.

Composite membranes composed of basic substrates doped with inorganic proton donors have recently attracted much attention due to their high proton conductivity, chemical and electrochemical stability at high temperature in addition to facile processing procedure.[4] Phosphoric acid (PA) is one of the most attractive inorganic proton donors that have been found to maintain high conductivity and reasonable stability at elevated temperature.[5] A typical example is commercial PA doped polybenzimadazole (PBI) membranes, which have been subjected to frequent investigations and showed reasonable performance in PEMFC at 190 °C without any additional humidification However, such membranes are vulnerable to degradation partially caused by fragility and electrolyte leaching.[7]

Alternatively, PA membranes prepared by doping of precursor films obtained by radiation-induced grafting (RIG) of heterocyclic monomers such as 4-vinylpyridine (4-VP) and 1-vinylimidazole (1-VIm) onto poly(ethylene-co-tetraflouroethylene) (ETFE) were reported in literature and found to be an attractive materials for HT-PEMFC.[8,9] Compared to conventional membranes preparation methods, the use of RIG simplifies the procedure, allows composition and properties control and provides solution for film formation as reaction starts form pre-existing sheets.[10] 1-VIm monomer was selected to provide a basic centre (-N$^+$-) resembling imidazole ring of PBI to conduct protons at temperatures above 100 °C when protonated by doping with PA. On the other hand, the selection of ETFE film as a base polymer was motivated by its outstanding properties including chemical inertness, thermal stability and mechanical integrity in addition to high-radiation resistance.[11]

In a previous brief communication the analysis of the properties of one proton conducting membrane (54% degree of grafting) obtained by RIG of 1-VIm onto ETFE film followed by PA acid doping was reported.[12] However, details of effects of grafting parameters on G% in the membrane precursor and PA doping parameters on the acid loading levels in the final membranes were not reported. Moreover, a detailed investigation for the effect of doping level, temperature, relative humidity on the proton conductivity of such membranes using DC impedance technique has not been yet reported. The objectives of present article is to report a systematic investigation of the effects of variation of: i) radiation grafting parameters on the content of poly (1-VIm) in grafted precursors i.e. G%, ii) PA treatment parameters (time, acid concentration, G% and temperature) on the doping level in the membranes and iii) G%, temperature, relative humidity (%RH) on the proton conductivity of the membranes.

2.0 EXPERIMENTAL

2.1 Materials

ETFE film (125 μm thickness and 1.69 g/cm^3 density) was supplied by Good fellow (Cambridge, England). 1-VIm of purity >99% was purchased from Fluka (Switzerland) and used without further purification. 37% Hydrochloric acid (37%) and 85% phosphoric acid (85%) were obtained from J.T. Bakers (Philipsburg, NJ, USA). A deionized water of of 18 MΩ produced using (NANOpure® DIamond™) water purifier was also used in all experiments.

2.2 Preparation of Membrane

The ETFE film was cut into samples of 5 cm x 5 cm, washed with ethanol and dried in a vacuum oven. The film samples were kept under vacuum in sealed thin polyethylene bags prior to irradiation using a universal electron beam (EB) accelerator (NHV-Nissin High Voltage, EPS 3000, Cockroft Walton type, Japan) operated at an acceleration voltage of 2 MeV and 10 kGy per pass. The film was irradiated to a total dose in the range of 20-100 kGy. After irradiation, the film was kept in a low temperature freezer at -65°C for a day.

The grafting reaction was carried out by introducing monomer solutions diluted with water in the range of 20-100 vol% (1-VIm/H_2O) and bubbled with purified N_2 gas for 30 min. to evacuate the vessel containing irradiated ETFE samples using as reported elsewhere.[12] The reaction was allowed to continue for a time in a range of 1-24 h at temperatures in the range of 30-75°C. After grafting, the grafted films were extracted in 0.1M HCl solutions under sonication to remove the poly(1-VIm) homopolymer and unreacted 1-VIm. The degree of grafting (G%) in the samples (membrane precursors) was calculated as follows:

$$G(\%) = \frac{m_g - m_o}{m_g} \times 100 \qquad (1)$$

where, m_g and m_o are the weights of the grafted and original ETFE films, respectively.

The grafted precursor films were doped with PA under N_2 atmosphere in a glass reactor. The acid concentration was varied from 30-60% at temperatures in the range of 5-100°C for doping time periods varied from 1 to 5 days. Later, the membranes were extracted and rinsed in a deionized water to remove the excess acid. The membranes were removed and dried for 16 h at 80°C in a vacuum oven. Finally, the dried membranes were weighted and the acid doping level per polymer repeating unit (X_d) was calculated as follows:

$$X_d = \frac{(w_d/100) \times M_p \times (1 + w_i)}{M_d \times (1 - (w_d/100)) \times w_i} \qquad (2)$$

where, X_d is the doping level [mmol PA/repeat unit of poly(VIm)], w_d is the mass fraction of the dopant, M_p is the molar mass of the repeating unit (g/mol), w_i is the percentage of weight increase of the grafted films and M_d is the molar mass of the dopant (g/mol).

2.3. Fourier Transform Infrared Measurements

Fourier transform infrared (FTIR) measurements of samples were recorded on a Nicolet 5700 spectrophotometer in a transmittance mode at a frequency range of 500-4000 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were detected and analysed using Essential FTIR™ commercial software.

2.4. Differential Scanning Calorimetry Measurements

Differential scanning calorimetry (DSC) measurements were recorded on a Mettler Toledo DSC 822 thermal analyzer under N_2 atmosphere in a temperature range of 50-300°C at a constant heating rate of 20°C/min. The degree of crystallinity (Xc) of the grafted films was calculated by taking the heat of melting of 100% crystalline of ETFE into account and correcting their recorded heat of melting by dividing over the weight fraction of ETFE in the grafted films and PA doped membranes as described elsewhere.[13]

2.5. Thermal Gravimetric Analysis Measurements

Thermal gravimetric analysis (TGA) of the films was performed using a Mettler Toledo TGA/SDTA 851 thermal analyzer. All the heating runs were made under N_2 atmosphere in a temperature range of 50-700°C at a constant heating rate of 20°C/min.

2.6. Conductivity Measurements

The ionic conductivity of the membrane was measured at a temperature range of 30-120°C using a 4-probe conductivity cell (BT-175) from BeckkTech. (Loveland, CO, USA) equipped with thermocouples and temperature controller. The cell was connected to a DC source meter (Keithley 2400, Cleveland, OH, USA) and humidity control system and the whole set-up was controlled by Lab view software. The membrane was cut into strips of 3 mm x 350 mm size, which was clamped between the platinum electrodes and placed in the externally insulated conductivity cell. The relative humidity (RH%) inside the conductivity cell was maintained in the range of 20-100% by means of pre-conditioned humidified N_2. The gas conditioning was performed using a humidification system equipped with humidifier, temperature controller, and thermocouple as well as gas flow meter. The relative humidity was detected by a humidity sensor attached to the conductivity cell and interfaced with the computer. The ionic conductivity (σ, S/cm) was calculated according to the following equation:

$$\sigma\ (S/cm) = L / (R \cdot W \cdot T) \qquad (3)$$

where, W is width of the membrane sample (cm), T is the thickness (cm), R is the resistance (Ω) and L is the distance between probes (cm).

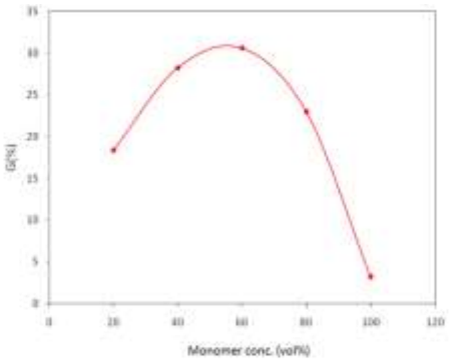


Figure 1 Variation of the degree of grafting with monomer concentration. Grafting conditions are: absorbed dose, 100 kGy; grafting temperature, 60°C and grafting time, 16 h.

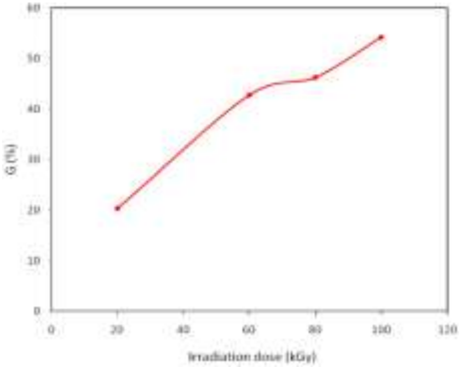


Figure 2 Variation of the degree of grafting with the irradiation dose. Grafting conditions are: monomer concentration, 60 vol%; grafting temperature, 60oC and grafting time, 16 h.

3.0 RESULTS AND DISCUSSIONS

3.1. Parameters Affecting Content of Grafted Moiety (G%)

Figure 1 shows the relation between the monomer concentration and G% 1-VIm onto ETFE film. G% was found to increase steeply with the increase in the monomer concentration and achieved a maxima at 60 vol% beyond which it dropped sharply until it reached its lowest value at 100 vol%. The increasing trend of G% up to 60% 1-VIm concentration is due to the increase in the amount of monomer diffused to the grafting sites leading to the enhancement of grafting reaction. On the other hand, the sharp decrease beyond 60 vol% 1-VIm concentration is due to the increase in the medium viscosity near the grafting sites. This is most likely caused by the growing tendency of some monomer molecules to homopolymerize leading not only to partial consumption of monomer molecules in a side reaction but also to hindrance of the diffusion of the monomer molecules and eventual prevention from reaching radicals located in the inner layers. The effect of monomer in this study agrees very well with that obtained earlier in similar grafting systems (1-VIm/ETFE).[8] Grafting of other vinyl monomers such as styrene onto ETFE films also showed similar parabolic trend.[14]

Figure 2 shows the relation between the absorbed dose and G%. The increase in the absorbed dose led to a gradual and continuous increase in G%. This behaviour is due to the increase in the amount of radicals formed in the ETFE film leading to the involvement of more radicals in the grafting reaction. Combining the effect of monomer concentration and with dose results, it can be suggested that G% in the present grafting system is a function of amount of radicals formed in the polymer films and the concentration of the monomer available in the grafting sites.

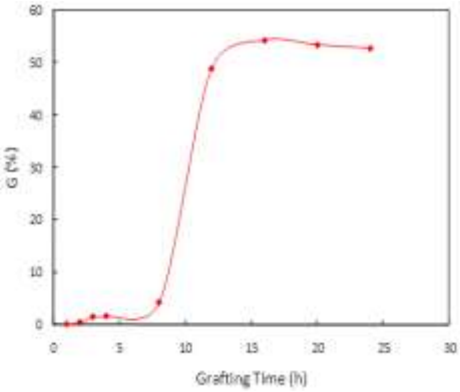


Figure 3 Variation of the degree of grafting with the reaction time. Grafting conditions are: monomer concentration, 60 vol%; absorbed dose, 100 kGy and temperature, 60oC.

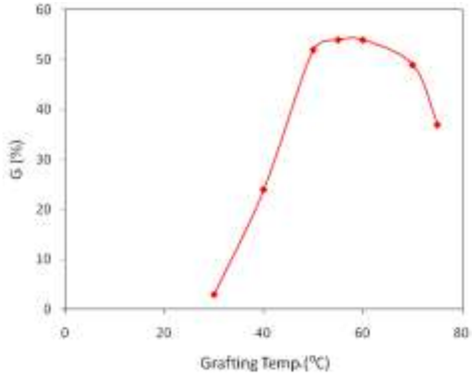


Figure 4 Variation of G% with reaction temperature. Grafting conditions are: monomer concentration, 60 vol%; absorbed dose, 100 kGy and reaction time, 16 h.

The variation of G% with the grafting time is presented in Figure 3. It is clear that the rate of grafting increased slowly in the first 8 h and this was caused by the slow diffusion of the monomer through film surface layers leading to low Gs% and suggesting that grafting at this point of time remained confined to the film surfaces. This was followed by a sharp increase up to 16 h suggesting that surface grafted layers were swollen in the monomer solution in a way facilitating the diffusion of more monomer molecules to the grafting sites. As the time further increased, G% reached a plateau achieving a grafting saturation. A maximum G% of 54% was obtained at 16 h.

Figure 4 shows the variation of G% with the reaction temperature for grafting of 1-VIm onto ETFE film. As can be obviously seen, G% sharply increased with the increase in the temperature until achieving a maximum value at 60 °C, beyond which it remarkably dropped. The drastic increase in G% up to 60 °C can be attributed to the increase in the amount and the reactivity of the thermally decomposed trapped radicals in irradiated films. This is coincided with an increase in the monomer diffusion to the grafting sites leading to an enhancement in the initiation and propagation rates couple with a delay in the chain termination. As the temperature further increased a mutual recombination of the activated radicals and bimolecular termination of the graft growing chains mostly took place lowering G%. The temperature effect on G% in this study is similar to that for grafting of styrene and 4-vinylpyridine onto ETFE films.[14,15]

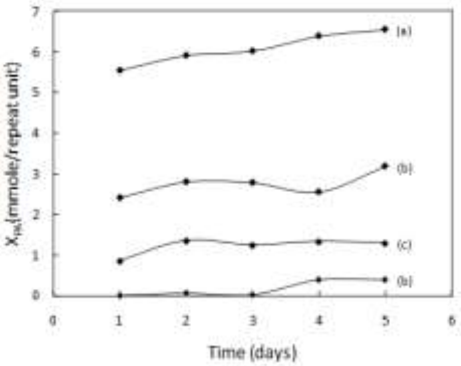


Figure 5 Variation of doping level in membrane with doping time at a temperature of 30°C for ETFE membranes having various G%: (a) 54%, (b) 38%, (c) 20% and (d) 8%.

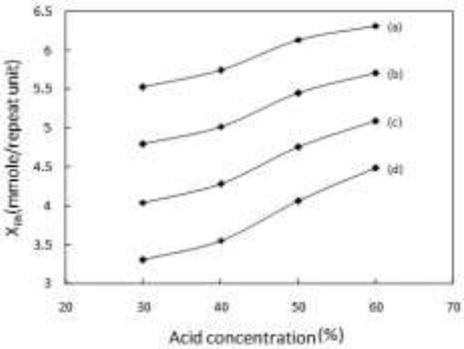


Figure 6 Variation of doping level in membrane with acid concentration in doping solution at a temperature of 30°C for ETFE membranes having different degrees of grafting: (a) 54%, (b) 38%, (c) 20% and (d) 8%.

3.2. Parameters Affecting Level of Acid Doping Reaction

The variation in the acid doping level with treatment time at a temperature of 30°C for membranes having various G% is shown in Figure 5. The doping level was found to increase with the time and tends to level off after 4 days for all grafted samples. The doping values were found to be 0.3, 1.29, 3.18 and 6.55 mmol/repeat unit for 8, 20, 38 and 54% grafted precursors, respectively. The doping behaviour seems to follow a front mechanism in which PA dopent react with =N- of the imidazole ring of poly(1-VIm) available on the surface of the grafted films then progress inwards as function of time until all available imidazole rings in the membranes were fully occupied after 5 days.

Figure 6. shows the variation of doping level in the membrane with PA concentration in the solution for grafted ETFE membrane having various G% for 5 days doping time. The doping level was found to increase with the increase in the dopant concentration and this is due to the availability of more ionized acid molecules in the solution that causes more interactions with =N- of the imidazole ring of poly (1-VIm). It is important to mention the quality of the membrane doped with PA at 60% acid concentration is less than those doped at 50% PA concentration and therefore the latter PA concentration was used in all doping of all samples.

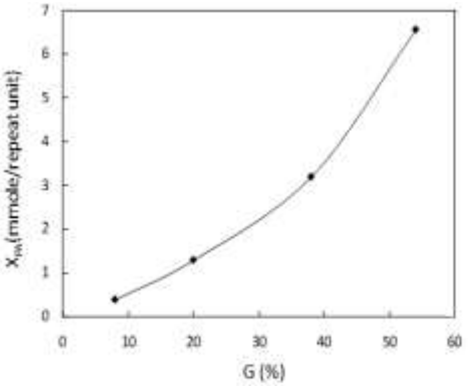


Figure 7 Variation of doping level in membrane with G% of ETFE membranes at 30°C and 50% phosphoric acid concentration for 5 days doping time.

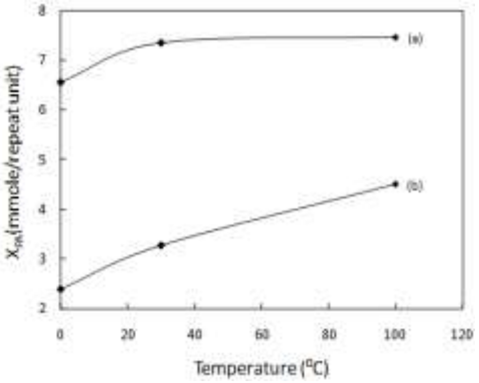


Figure 8 Variation of doping level with doping temperature for ETFE grafted membranes (a) 54% and (b) 38% for 50% phosphoric acid concentration for 5 days doping time.

The relation between the doping level and G% at constant PA concentration of 50% and 5 days doping time is illustrated in Figure 7. It can be seen that the increase in G% in membrane precursor leads to an exponential increase suggesting that the PA doping level rise is directly proportional to the increase in G%. This behaviour can be attributed to the gradual increase of the amorphous phase inside the membranes caused by the growing of the poly(VIm) content to the ETFE matrix, which perceived more acid swelling that facilitated the interaction of more PA with the nitrogen centres of the imidazole rings.

Figure 8. shows the variation of doping level with temperature for two important membranes having G% of 54 and 38% doped for 5 days. It is clear that, the doping level increased with the increase in the temperature until achieving a maximum value at 100°C in both membranes. However, the accelerating effect of the temperature is found to be more pronounced in the membrane having G% of 38% than that of 54% at temperature higher than 30°C. The increase in the doping level with the temperature can be generally attributed to the increase in the acid diffusion rate,

which accelerates the progressive reaction with =N- of the grafted poly(VIm). The presence of more grafted layers in 54% membrane accelerated the reaction in a way that consumed most of the available basic =N- forming complexes with PA at a temperature 30°C beyond which the rate of doping was remarkably lowered. Unlikely, the diffusion rate and the reaction were slowed by presence of less grafted layers in 38% grafted membrane at 30°C after which the increase in the temperature to 100°C remarkably enhanced the rate of acid diffusion and the doping level. These results suggest that the final doping level in the membrane depends strongly upon the acid concentration, G% and doping medium temperature. Moreover, doping at room temperature is preferable at high G% while achieving high doping level can be obtained at high temperatures for membranes with low G%.

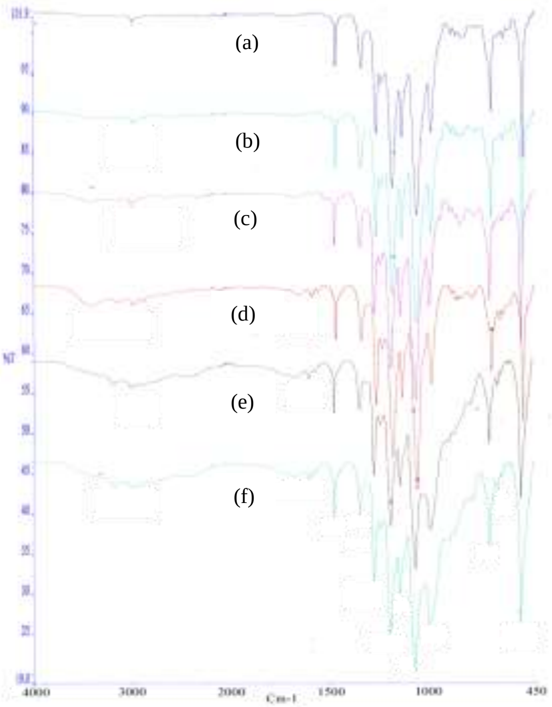


Figure 9 FTIR spectra of: (a) pristine ETFE film, (b) 8% grafted ETFE, (c) 38% grafted ETFE, (d) 54% grafted ETFE films and corresponding (e) 38% grafted and PA doped and (f) 54% grafted and PA doped membranes.

3.3. Chemical Evidence of Grafting and Acid Doping

To provide an evidence for grafting 1-VIm and PA doping, FTIR analysis was performed on the PA doped membranes in comparison with their corresponding grafted and original ETFE films as illustrated in FTIR spectra presented in Figure 9. The spectrum of original ETFE film is identified by the presence of a number of strong bands in the range of 1000-1400 cm^{-1} representing C-F of CF_2 groups together with a small band representing stretching vibration of CH_2 at 2915 cm^{-1}. The grafted films displayed a number of characteristic bands representing -CN and -CH at the ranges of 1525-1575 and 725-880 cm^{-1}.[9] The bands at 2750–3180 and 3250–3650 cm^{-1} were respectively assigned for N–H and C–H of the grafted imidazole rings, which are involved with traces of moisture involved in H-bonding. The intensity of all characteristic bands was found to increase with the increase in G%. The spectra of PA doped membranes showed broad bands in the range of 2100-3600 cm^{-1} represent the transmittance of a network of hydrogen bonds associated with PA. For instance, the stretching vibration of N-H bonds of the imidazole rings was shifted from 3180 cm^{-1} to 2880 cm^{-1} and this is due to the formation of N–H–O- and O–H–O- caused by the introduction of PA. The broad bands at 2350 cm^{-1} can be assigned to the stretching vibration of imidazolium NH^+ protonated by the dopant.[8,9] This trend agrees completely with the behaviour of other PA membranes reported in the literature and can be attributed to the formation of H-bonding and hydrogen phosphate groups. Hence, it is confirmed that PA doped membranes were successfully prepared by grafting of 1-VIm and subsequent doping with phosphoric acid.

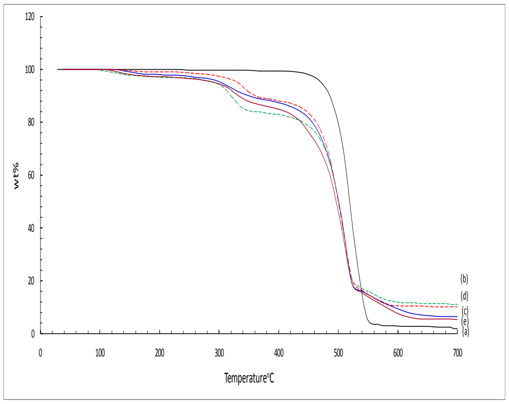


Figure 10 TGA thermograms of: (a) pristine ETFE film (b) 38% grafted ETFE film and (c) corresponding PA doped membrane together with (d) 54% grafted ETFE film and (e) corresponding PA doped membrane.

3.4. Thermal Stability

Figure 10 presents the TGA thermograms of PA doped membranes in comparison with their corresponding grafted and original ETFE films. The original ETFE film shows a single-step degradation pattern at 435°C unlike the grafted ETFE films, which showed a three-step degradation pattern at 128, 322 and 435°C, respectively. The degradation started with the dehydration of the moisture traces associated with imidazole rings by H-bonding followed by the decomposition of poly(VIm) and the degradation of ETFE molecular chains. These results suggest that the grafted poly(VIm) is not compatible with the molecular chains of ETFE backbone leading to the formation of phase separated domains as indicated by the transitions at 322 and 435°C, respectively. The PA doped membranes also displayed a three-step degradation pattern started at 120, 321 and 420°C due to dehydration that starts at a lower temperature than grafted film, continuous decomposition of the grafted poly(VIm) coupled with the deacidification and decomposition of ETFE molecular chains, respectively. The beginning of degradation of the membrane was found to be 8°C lower than (120°C) that of the grafted film (128°C) and this is due to the higher moisture content in the PA doped membranes. The absence of any distinction between the decomposition transitions of poly(VIm) and that of PA is due to their close thermal degradation temperatures. These results are in a good agreement with similar PA doped membranes obtained by grafting various basic vinyl monomers onto fluorinated polymer films.[8,15] From the TGA results, it can be suggested that the membrane is suitable for testing in a high temperature PEM fuel cell up to 200°C.

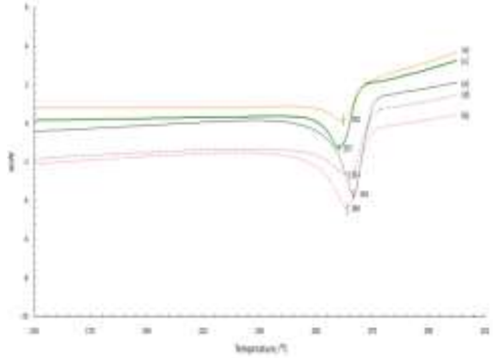


Figure 11 DSC thermograms of: (a) pristine ETFE film (b) 54% grafted ETFE film and (c) corresponding PA doped membrane together with (d) 38% grafted ETFE film and (e) corresponding PA doped membrane.

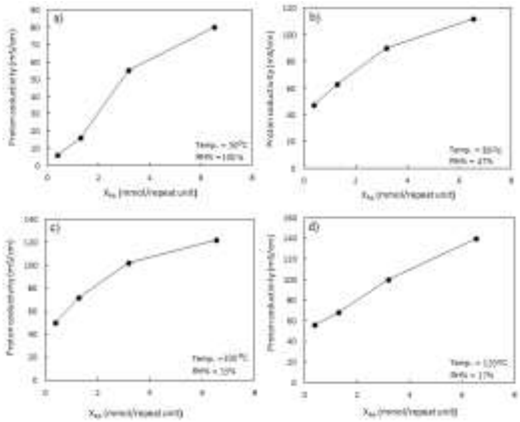


Figure 12 Variation of proton conductivity with acid doping level at various temperatures: a) 30°C, b) 80°C, 100°C and 120°C and relative humidity: 100%, 47%, 35% and 17% for PA doped poly(VIm) grafted membranes.

3.5 Thermal and Structural Properties

Figure 11 shows DSC thermograms of the doped PA membranes in comparison with their corresponding grafted and original ETFE films. The data of the melting temperature (T_m) and the degree crystallinity (X_c) obtained and calculated from thermograms are presented in Table 1. T_m of the original ETFE film was captured at 263°C, which was shifted to 262 and 260°C after grafting of 1-VIm and subsequent PA doping. This was accompanied by a parallel down shift trend in Xc of ETFE backbone. The decrease in T_m and X_c was raised by the increase in G% and the subsequent acid doping. The slight shift in T_m suggests a minute partial disruption developed during membrane preparation procedure (grafting and doping). Moreover, the reduction in the melting peak area are substantially due to the dilution of the crystalline structure of ETFE matrix with the amorphous poly(VIm) grafts. These observations are going pretty well with the calculated X_c, which showed a reduction from 34.2 in the original ETFE film to 27.5 and 25.2 in 54% grafted ETFE films and PA doped membranes, respectively. Thus, the reduction in T_m an X_c of the grafted and PA doped membranes can be reasonably attributed to 'dilution effect'. Such effect resulted from the incorporation of amorphous poly(1-VIm) coupled with a limited disruption in the inherent crystallities of ETFE film as indicated by the shift in T_m.[15] The PA doping further decrease the dilution of the crystalline structure leading further reduction in T_m and X_c. Nevertheless, the membranes maintain a reasonable level of X_c despite the dilution effect coupled by the minor disruption in its crystalline structure of ETFE film.

Table 1 Variation of melting temperature and degree of crystallinity with VIm grafting and PA acid doping

Samples	T_m	X_c
Original ETFE films	263	34.2
38% grafted film	262	28.4
54% grafted film	261	27.5
38% grafted and PA doped membrane	260	26.3
54% grafted and PA doped membrane	257	25.2

3.6 Ionic Conductivity

Figure 12 (a-d) shows the variation of proton conductivity with the acid doping level at various temperatures and RH%. It can be observed that the conductivity of all membranes gradually increases with the increase in the acid doping level at all temperatures and RH% values. For instance, the proton conductivity increased with the increase in the temperature from 30-120°C and the reduction in RH% from 100 to 17%. To explain this trend, it is necessary to understand the way proton conductivity takes place in these membranes. The doping of poly(VIm) grafted film with PA led the formation of $-NH^+$ proton donor sites in the membranes causing H^+ hopping to take place between $-NH^+$ sites and PA anions leading to continuous proton transfer. The increase in acid doping level increases the level of water molecules associated with PA by H-bonding. This allows other PA ionic species such as $H_2PO_4^-$ to contribute to the proton transfer leading to a remarkable increase in conductivity. As the temperature increases, the proton hopping increases leading to higher proton conductivity. The increase in the proton conductivity with the decrease in RH%, suggests that PA doped membranes obtained in this study is less-water dependent. These results agree very well with the observation made by He et al.[16] who reported that the acid molecules are bridging the phosphate and imidazole moieties allowing proton hopping even at low RH% levels. Moreover, PA as a dopant exerts effective proton conductivity even in an anhydrous form, due to its unique proton conduction mechanism by self-ionization and self-dehydration. The effect of temperature, G%, and acid doping level reported for the present membranes are going along with those reported for PA doped PBI.[5]

4.0 CONCLUSIONS

PA doped proton exchange membranes with reasonable properties were successfully prepared by RIG of 1-VIm onto ETFE films and subsequent acid doping. The content of poly(1-VIm) in the membrane precursor was found to be a function of the grafting parameters. The acid doping level (mole of PA per polymer repeating unit was found to be dependent on reaction parameters such as time of reaction, acid concentration, G% and doping temperature. The membranes were found to have multistage degradation patterns with a thermal stability up to 200°C. Grafting of 1-VIm and subsequent acid doping was found to affect T_m and X_c of the membranes However, all membranes were found to retain a reasonable level of crystallinity sufficient to maintain the physical strength necessary for the use as a polymer electrolyte in HT-PEMFC. The proton conductivity of the membranes was found to be dependent on doping level, temperature and RH%. Proton conductivities of 56, 68, 100 and 140 mS/cm at temperature of 120°C and RH% of 17% were achieved for membranes having acid doping level of 0.39, 1.28, 3.19 and 6.54 mmol/polymer repeat unit corresponding to G% of 8, 20, 38 and 54%, respectively. The high proton conductivity at low RH% suggests that the obtained membranes are less-water dependent. It can be concluded that composite acid/base membranes obtained in this study have a strong potential for testing in PEM fuel cell operated above 100 °C.

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References

[1] Çelik, S. Ü., A. Bozkurt, S.S. Hosseini. Alternatives toward proton conductive anhydrous membranes for fuel cells: Heterocyclic protogenic solvents comprising polymer electrolytes, *Progress in Polymer Science*. 37: 1265– 1291.

[2] Bose, S., T. Kuila, T. X. H. Nguyen, N. H. Kim, K. Lau, J. H. Lee. 2011. Polymer membranes for high temperature proton exchange membrane fuel cell: Recent advances and challenges. *Progress in Polymer Science*. 36(6): p. 813-843.

[3] Dupuis, A.-C. 2011. Proton exchange membranes for fuel cells operated at medium temperatures: Materials and experimental techniques. *Progress in Materials Science*. 56 (3): 289-327,

[4] Yang, Y., A. Siu, T.J. Peckham. S. Holdcroft S. Structural and morphological features of acid-bearing polymers for PEM fuel cells. *Advances in Polymer Science*. 2008; 215: 55-216.

[5] Glipa, X., B. Bonnet, B. J. Mula, D. Jones, J. Roziere. 1999. Investigation of the conduction properties of phosphoric and sulfuric acid doped polybenzimidazole. *Journal of Materials Chemistry*. 9: 3045-3049.

[6] Kawahara, M., J. Morita, M. Rikukawa, K. Sanui, N. Ogata. 2000. Synthesis and proton conductivity of thermally stable polymer electrolyte: Poly(benzimidazole) complexes with strong acid molecule. *Electrochimica Acta*. 45: 1395-1398.

[7] Li, Q. F., R. He, J. O. Jensen, N. J. Bjerrum. 2003. Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C. *Chemistry of Materials*. 15: 4896-4915.

[8] Schmidt, C., G. Schmidt-Naake. 2007. Proton conducting membranes obtained by doping radiation-grafted basic membrane matrices with phosphoric acid. *Macromolecular Materials and Engineering*. 292: 1164-1175.

[9] Nasef, M. M., A.A. Aly, H. Saidi, A. Ahmed. 2011. Optimization of reaction parameters of radiation induced grafting of 1-vinylimidazole onto poly(ethylene-co-tetraflouroethene) using response surface method. *Radiation Physics and Chemistry*. 80: 1222-1227.

[10] Nasef, M. M., O. Guven. 2012. Radiation-grafted copolymers for separation and purification purposes: status challenges and future directions, *Progress in Polymer Science*. 37 (12) 1597–1656.

[11] Nasef, M. M., H. Saidi. 2003. Electron beam irradiation effects on ethylene- tetrafluoroethylene copolymer films. *Radiation Physics and Chemistry*. 68: 875-883.

[12] Nasef, M., A. A. Aly, H. Saidi. 2013. Composite proton conducting membrane by radiation induced grafting of 1-vinylimidazole onto poly(ethylene-co-tetrafluoroethylene) and phosphoric acid doping. *High Performance Polymers*. 25 (2): 196-202.

[13] Nasef M. M., H. Saidi. 2004. Structure of polyethylene-graft-polystyrene sulfonic acid membranes prepared by radiation-induced grafting. *International Journal of Polymeric Materials*. 53: 1027-1043.

[14] Rohani, R., M. M. Nasef, H. Saidi, K.Z.M. Dahlan. 2007. Effect of reaction conditions on Electrons induced graft copolymerization of styrene onto poly(ethylene-co-tetrafluoroethylene) films: kinetics study. *Chemical Engineering Journal*. 132, 27-35.

[15] Nasef, M. M., E. Shamsaei, H. Saidi, A. Ahmad, K. Z.M. Dahlan. 2013. Preparation and characterization of phosphoric acid composite membrane by radiation induced grafting of 4-vinylpyridine onto poly(ethylene-co-tetrafluoroethylene) followed by phosphoric acid doping. *Journal of Applied Polymer Science*. 128 (1): 549-557.

[16] He, R., Q. Che, B. Sun. 2008. The Acid Doping Behavior of Polybenzimidazole Membranes in Phosphoric Acid for Proton Exchange Membrane Fuel Cells. *Polymers*. 9: 679-684