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Novel Acid-Base Poly vinyl chloride-Doped Ortho-Phosphoric Acid Membranes for Fuel Cell Applications

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Novel acid-base poly vinyl chloride –doped ortho-phosphoric acid membranes for prospective fuel cells (DMFC) applications were prepared for the first time. Base polymers were prepared first through amination using ethylene daimine (EDA). The base aminated PVC membranes were consequently doped with ortho-phosphoric acid (OPA). The later are significantly contributed to enhance ion exchange capacity (IEC) and thermal stability. Changes of chemical structure were verified through FT-IR, and TGA characterization. As a result, the thickness and the water uptake of acid-base prepared membranes were increased with increase of doped OPA concentration comparing with original PVC membrane. Maximum water uptake of 105(%) and 3.41 (meq/g) IEC were obtained. This makes the prepared acid-base PVC-doped OPA membranes promising and attractive new materials in fuel cells applications.

Keywords: Fuel Cell, Acid-Base Membranes, PVC, Ion Exchange Capacity

1. INTRODUCTION

It is generally accepted that proton exchange membrane fuel cell (PEMFC) is an energy-efficient and environmentally benign power source [1]. It has the potential to replace the internal combustion engines in vehicles and to provide the power for stationary and portable power applications. One of the vital components in PEMFC is proton exchange membrane, serving as a physical separator between the anode and the cathode with the functions of transporting proton and blocking electron. Currently, the most widely used and successful proton exchange membranes have been proved as per fluorinated copolymers with sulfonic acid functionalized side chains, such as Nafion^{TM} (DuPont), Aciplex^{TM} (Asahi) and Dow^{TM} (Dow) [2]. They exhibit high proton conductivity, good thermal stability, excellent chemical stability and adequate mechanical property for fuel cells running below 90 $^{\circ}$C. However, due to the complicated synthesis procedures, cost of the membranes is too high for commercial applications. Therefore, many efforts have been expended in developing the substitutes of the per fluorinated membranes [3–8]. One interesting way is to prepare proton exchange membrane from preformed polymer film. The polymer film functions as hydrophobic host that constrains the membrane swelling in water and provides the mechanical strength and dimensional stability, and the functional property, i.e. proton conductivity, is introduced by (i) ionomer impregnation, or (ii) monomer grafting with subsequent sulfonation or (iii) monomer-impregnated polymerization with subsequent sulfonation. Gore-Select TM is a proton-conductive membrane made by ionomer impregnation, in which expanded polytetrafluoroethylene (ePTFE) is used as the substrate and Nafion solution as the ionomer [9, 10]. The reinforcement improves drastically the mechanical properties and the hydraulic permeation without sacrifice of the conductance. However, the impregnation is not particularly suitable for commercial manufacturing operations due to the difficulty of the hydrophilic polymer electrolyte solution penetrating into the hydrophobic pores of the ePTFE [11]. An alternative method is to hot-press two films of perfluorosulfonyl fluoride resin onto both sides of a microporous ePTFE sheet followed by the hydrolyzation of sulfonyl fluoride group ($–SO_2F$). There have been many researches on the monomer grafting method, and the grafting may be initiated by high-energy irradiation using γ-rays, electron-beam and swift heavy ions [12–14]. Several studies identify that poly (ethylenealt- tetrafluoroethylene) (ETFE), poly (vinylidene fluoride) (PVDF), poly (tetrafluoroethylene -co-hexafluoropropylene) (FEP), poly (tetrafluoroethylene-co- perfluoropropyl vinyl ether) (PFA) and cross linked polytetrafluoroethylene (cPTFE) are promising base polymers [14, 15]. Styrene is the most frequently used monomer due to its high thermal stability and moderate sulfonation process of the aromatic ring. However, sulfonated polystyrene is known to be susceptible to be attacked by radical species during fuel cell applications due to weakness of the benzylic alpha-hydrogen atom. Monomers with the higher intrinsic chemical stability, such as p-methyl styrene, p-tert-butylstyrene, α-methyl styrene, α, β, β-trifluorostyrene and its derivatives, have ever been used [14]. In the monomer-impregnated polymerization method, both porous and dense polymer films have been used. Yamaguchi et al. presented the principles where porous PTFE film was used as the substrate and acrylic acid as the monomer [16]. The polymerization was initiated by UV-irradiation. When dense polymer film was used, the monomer solution should be able to swell the polymer film. Choi et al. described the preparation principles where styrene was thermally polymerized within dense poly vinyl chloride (PVC) film [17, 18]. The PVC film was swollen in styrene solution. The monomer-absorbed PVC film permitted enlarged free volume due to the solvent effect. When the temperature was increased to the decomposition temperature of the initiator benzoyl peroxide (BPO), the monomer was polymerized within the PVC film. The propagated polystyrene chains were interpenetrated with those of the supporting film, and a physical network with semi-interpenetrating polymer network (semi-IPN) was formed. After sulfonation a cation exchange membrane was prepared. It was found that the prepared membrane had excellent electrochemical characteristics and could be properly used in electro dialysis.

In this article, acid-base PVC- doped OPA membranes for fuel cells applications were prepared and characterized for the first time. Aminated PVC base polymer was prepared first using EDA which consequently doped with OPA has a (–PO_3H) functional groups. The amination conditions, such as EDA concentration, reaction time and temperature were investigated. OPA doping conditions, such as OPA concentration, reaction time and temperature were investigated to have the optimum modification conditions. To follow up changes result from modification process, different characters were evaluated namely; water uptake, membrane thickness changes, ion-exchange capacity (IEC), FT-IR and TGA analysis.

2. EXPERIMENTAL

2.1. Materials

- Poly vinyl chloride (M. wt. ~48000**,** fine powder) belami fine chemicals. (India).
- Ortho-phosphoric acid (Purity 85% extra pure) Sigma- Aldrich Chemicals Ltd. (Germany).
- Ethylenediamin (Purity 99%) loba chemie (India).
- Tetrahydrofuran (THF) (Purity 99.9%) Sisco research laboratories (India).

2.2. Membrane preparation

Poly vinyl chloride (PVC) was dissolved in Tetrahydrofuran (THF) then reacted with Ethylenediamin (EDA). Factors affecting the amination process were studied with variation of EDA concentrations (1.5-7 %v/v) and reaction temperatures (25-65°C) for different time intervals (1-8 h). The aminated PVC membranes were then dissolved in Tetrahydrofuran (THF) and reacted with different concentration of Ortho-phosphoric acid (1.5-7.5 %v/v) at different temperatures (25-65°C) for different reaction time (1-8 h).

2.3. Membrane characterization

Water uptake (W %)

For membrane previously immersed in water at room temperature for 24 h, the surface was dried by wiping with filter paper and weighing. The obtained results are the average of three samples **[19]**.

$$W\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

W_{wet} and W_{dry} were the weights of the wet and dry membranes, respectively.

2.4. Dimensional changes (ΔA %)

After immersing the membranes into water at room temperature for 24 h, the area change were calculated from following equation **[20]**:

$$\Delta A\% = \frac{A - A_0}{A_0} \times 100 \qquad (2)$$

A_0 and A is the area of membrane before and after soaking treatment, respectively.

2.5. Infrared spectro-photometric analysis

Analysis of I.R. spectroscopic charts investing chemical structure original and modified membranes was carried out using Fourier Transform Infrared Spectrophotometer (Shimadzu FTIR-8400 S, Japan).

2.6. Thermal gravimetric analysis

TGA Analysis of original and modified membranes was carried out using Thermo-gravimetric Analyzer (Shimadzu TGA-50, Japan).

2.7. Ion Exchange Capacity

The ion exchange capacity (IEC) of the membranes was determined using acid–base titration. Weighed samples were immersed in 20 cm3 of a 2 M NaCl solution for at least 12 h at R.T. The solution was then titrated with a NaOH solution of known concentration. IEC was calculated as follows:

$$IEC(meq/g) = n(mmol/cm^3) \times v(cm^3)/w(gm) \qquad (3)$$

n, v, and w are the concentration of the NaOH solution, the titer of the NaOH solution, and the weight of the sample, respectively [21].

3. RESULTS AND DISCUSSIONS

3.1. Membrane preparation

3.1.1. Amination process

3.1.1.1. Effect of EDA Concentration

The effect of variation EDA concentration on the IEC is shown in Figure 1. It shows that there is an increase of IEC with increasing of EDA concentration from 1.5% to 3%. Maximum IEC was obtained at 3% EDA. Reaction of EDA' amine groups with PVC' secondary chlorine atoms results in formation of imide groups which represent doping sites for OPA. Increasing concentration of EDA increased the doped OPA and consequently the IEC. Beyond 3% EDA, no significant improvement in IEC was observed. This is may be due to substitute of all secondary chlorine atoms with amine groups using 3% EDA. According to the homogeneous reaction conditions of amination, no diffusion limitation effect on the reaction rate has been observed.

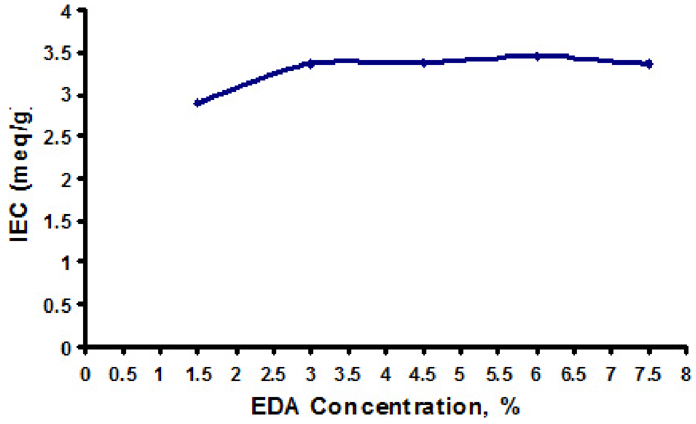

Figure 1. Effect of variation EDA concentration on the ion exchange capacity.

3.1.1.2. Effect of reaction temperature

The effect of variation amination temperature on the IEC was shown in Figure 2. The IEC was found almost constant with increasing reaction temperature from 25°C to 65°C. This is an indication for the absence of diffusion limitation and the low activation energy of the reaction between PVC's chlorine atoms and the amine groups of EDA.

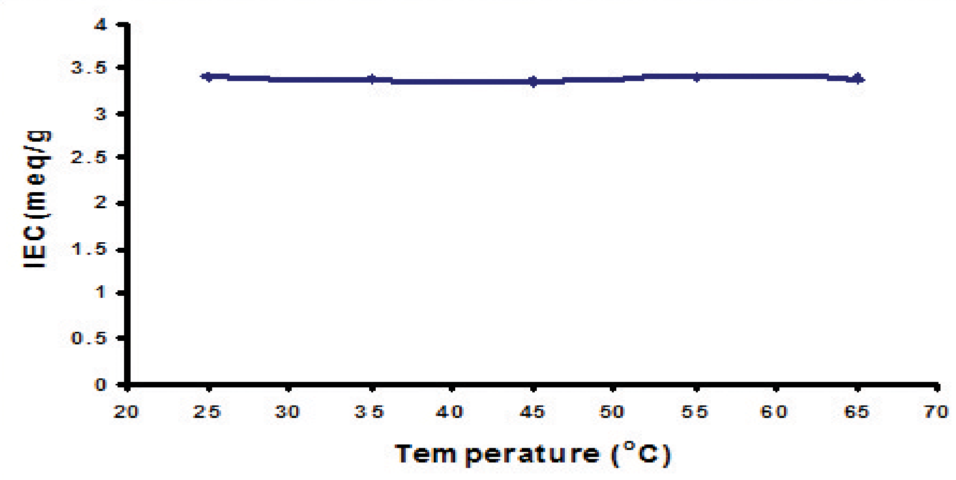

Figure 2. Effect of variation EDA' reaction temperature on the ion exchange capacity.

3.1.1.3. Effect of reaction time

The effect of variation amination reaction time on the IEC was shown in Figure 3. It shows that the IEC increases with increase time of reaction to reach maximum at 6 hours and then leveling off.

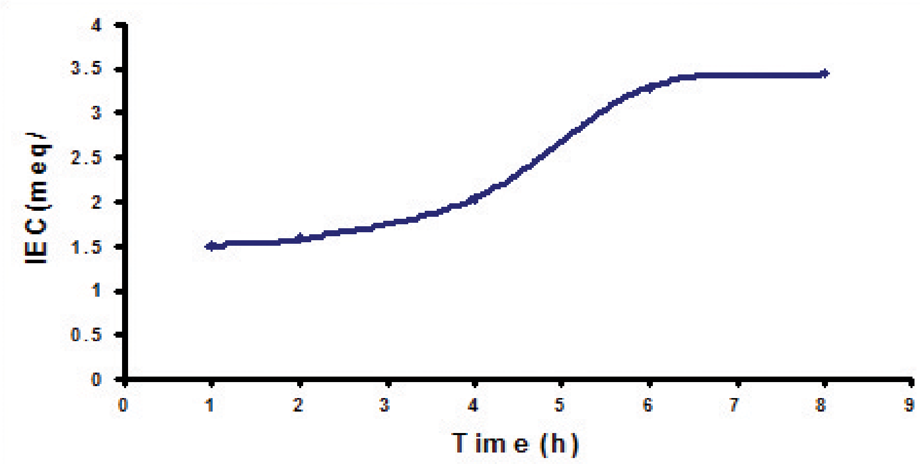

Figure 3. Effect of variation EDA amination' reaction time on the ion exchange capacity.

3.1.2. Phosphorization (doping) process

3.1.2.1. Effect of orthophosphoric acid concentration

The effect of variation orthophosphoric acid concentration on IEC was shown in Figure 4. The figure shows that there is an increment in IEC with increase of orthophosphoric acid concentration. Maximum IEC was obtained at 6% orthophosphoric acid and then leveled off. Increase OPA concentration will increase the doped OPA molecules which are responsible about IEC.

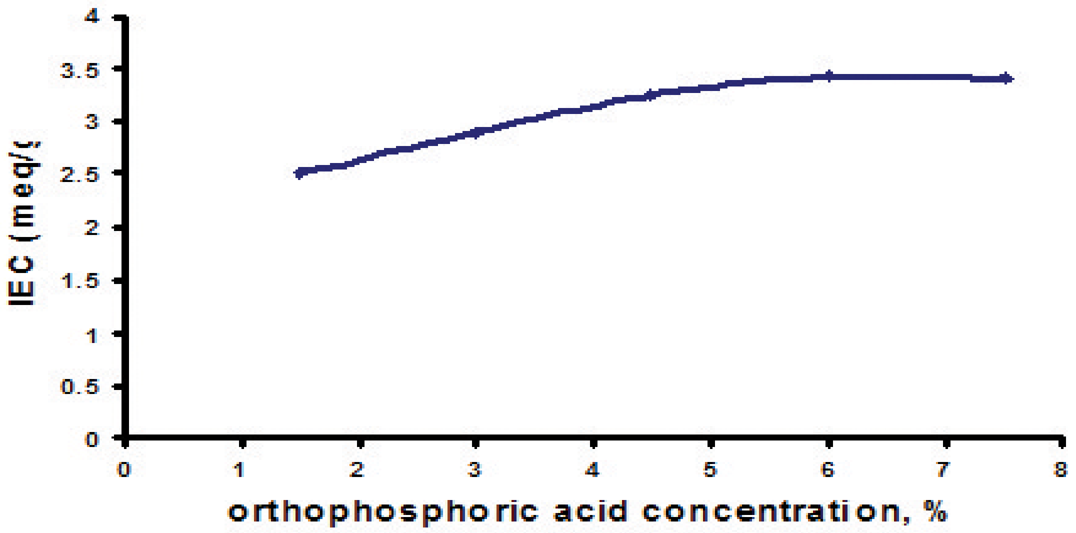

Figure 4. Effect of variation OPA on ion exchange capacity.

3.1.2.2. Effect of reaction temperature

The effect of variation OPA doping' temperature on the IEC was shown in Figure 5. In this figure it can be seen that the IEC has almost no changes with increasing doping' temperature from 25°C to 65°C. The absence of diffusion limitation due to carrying out the reaction in homogenous conditions eliminates the effect of temperature.

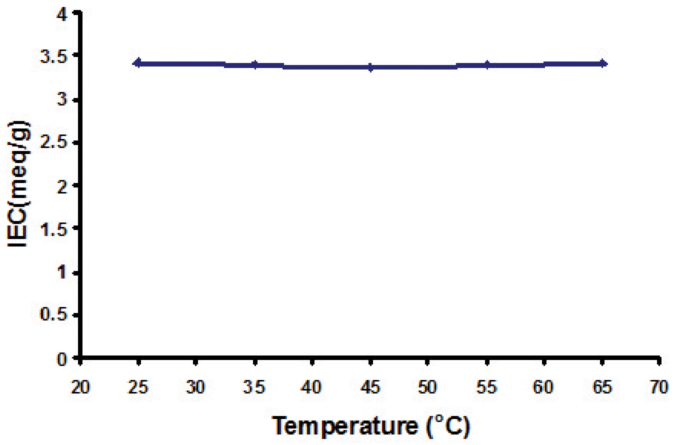

Figure 5. Effect of variation OPA doping' temperature on the ion exchange capacity.

3.1.2.3. Effect of reaction time

The effect of variation OPA doping' reaction time on the IEC was shown in Figure 6. The figure described that the IEC increases linearly with increase time of doping reaction. Increasing number of attached orthophosphoric acid molecules is the expected result. This automatically leads to increase the ion exchange capacity.

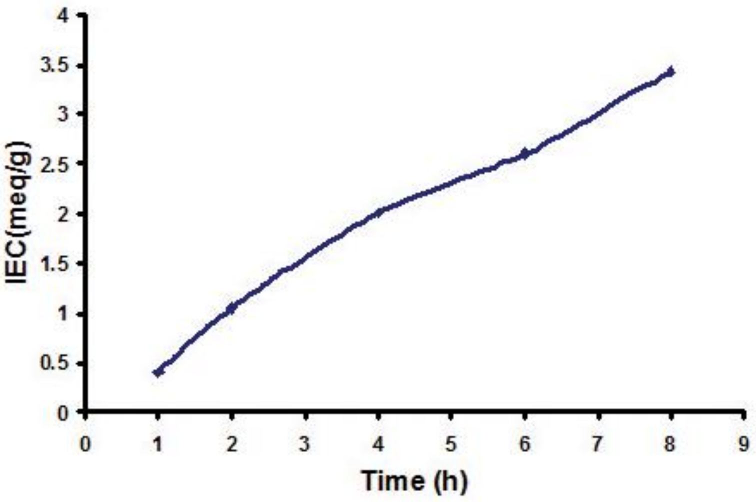

Figure 6. Effect of variation OPA doping' time on the ion exchange capacity.

3.2. Membrane characterization

3.2.1. Water up take (%)

The water content in polymer electrolyte membrane is one of the features for proton transport [22]**.** The water uptake of PVC membrane, aminated and OPA doped membranes was recorded in Table 1. From the table it is clear that the increase of water sorption of modified membranes over original PVC. This is due to the increase in the hydrophilic groups on the membrane which is represented by phosphoric groups. The obtained results reveal that variation of the preparation conditions enables us for having a wide range of water uptake membranes.

Table 1. Water uptake of original, aminated and OPA doped PVC membranes

Orthophosphoric acid concentration (%)	Water uptake (%)
Original PVC	0
1.5	31.78
3	34.99
4.5	56.57
6	69.07
7.5	105.54

3.2.2. Dimensions changes

The effect of the modification process on the dimensions changes of the modified membranes after their swelling in water for 24 h is presented in Table 2. The results showed that the dimensions changes were not significant in comparison with unmodified membrane, which confirms that the modification process has no impact on the dimension stability of the modified membranes. This is a good benefit of the used technology in our study in addition to the induced thermal and ion exchange capacity characteristics.

Table 2. Dimensions changes in water uptake for original and OPA doped PVC membranes.

Orthophosphoric acid concentration (%)	Dimension changes (%)
Original PVC	0
1.5	2.10
3	2.20
4.5	3.00
6	5.00
7.5	5.00

3.3. Membrane Thickness Changes

Figure 7 shows the changes in membranes thickness as measured by micrometer against the concentration of orthophosphoric acid. It's clear from the graph that the thickness of the membranes increases with increasing orthophosphoric acid concentration. The repulsion between negative charges of phosphoric acid groups results in repulsion between polymer chains. This leads finally to increase the membrane thickness.

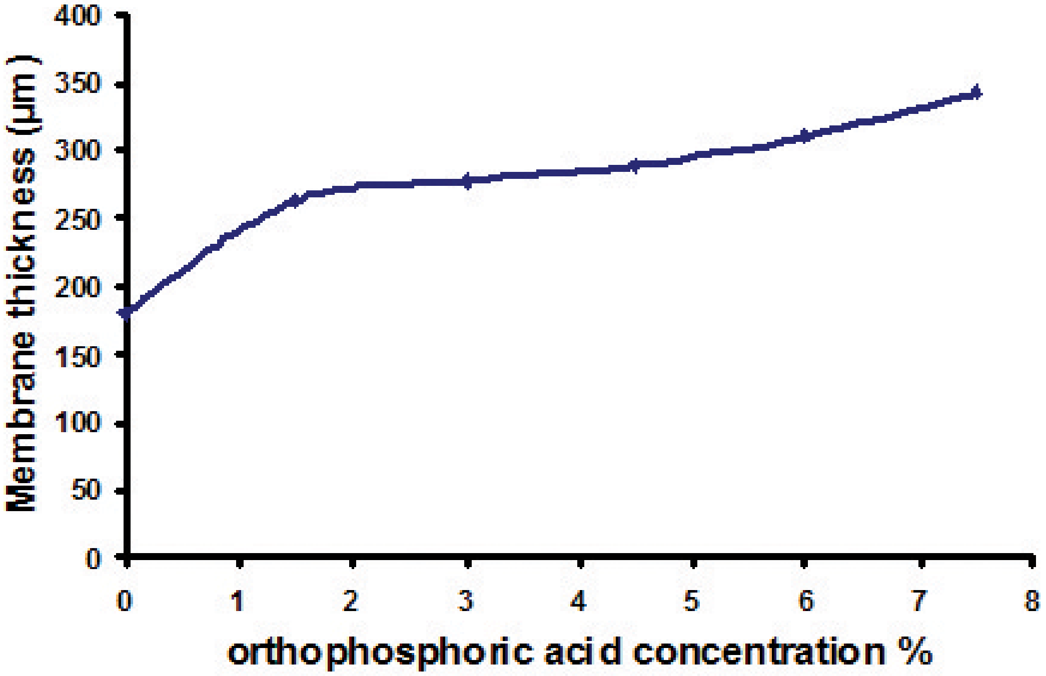

Figure 7: Effect of variation OPA concentration on the thickness of PVC-OPA doped membranes.

3.4. Infrared Spectrophotometric analysis

Figure 8 illustrates the FT-IR spectra for PVC, aminated, and PVC-OPA doped membranes. The IR spectrum of PVC membrane shows characteristic beaks (curve A) .The spectra for aminated PVC shows a new broad beak at 3357cm^{-1} which is corresponding to the presence of amine groups. With OPA doping, a very broad absorption band complex appears in the wave number range from about 2500 to 3000 cm^{-1} [23] (curve B-F).

3.5. Thermal gravimetric analysis

Thermal Gravimetric Analysis (TGA) of original PVC membrane**,** aminated and PVC-OPA doped membranes were carried out by thermo-gravimetric analyzer in nitrogen atmosphere at a heating rate of 20°C/min, as shown in Figure 9. For PVC membrane (curve A), it was found that there are two beaks which refer to weight loss. The fist one is at 374.4 ºC result from breaking of C-Cl bond and the other one is at 591 ºC for the ethylene bond. For aminated and PVC-OPA doped membranes, a new band appeared at 135 ºC which result from the evaporation of humidity resulted from converting the hydro-phobicity of the modified membranes. Also, it was found that the C-Cl band is shifted to 378.2 ºC which gives some stability to the membranes. The thermal stabilities for all modified membranes have been evaluated by measuring the weight loss percent at 500 °C in comparison with the virgin PVC.

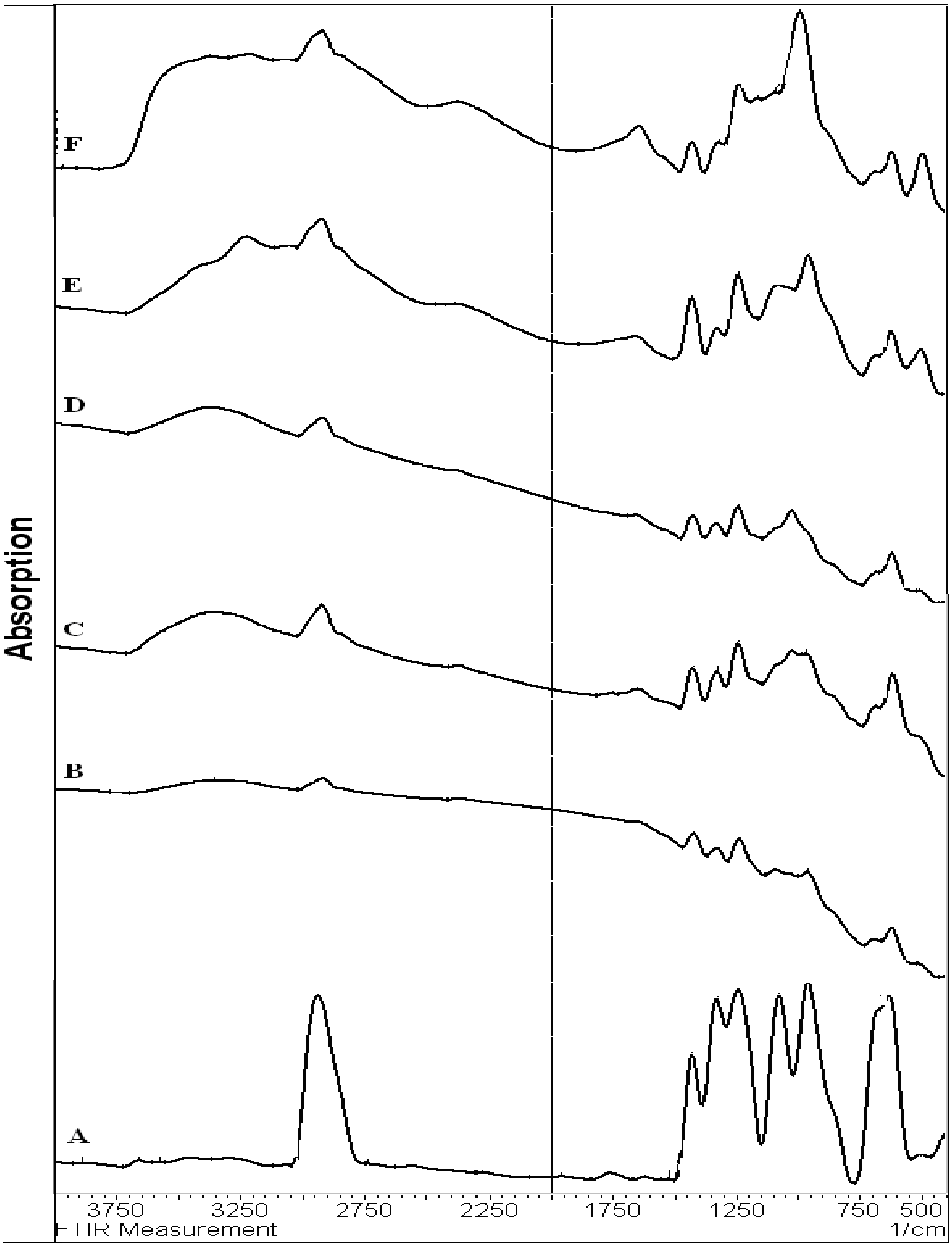

Figure 8. FT-IR Spectrum of: original PVC membrane (A), [6% EDA, .5% orthophosphoric acid (B)], [6% EDA, 3% orthophosphoric acid (C)], [6% EDA, 4.5% orthophosphoric acid (D)], [6% EDA, 6% orthophosphoric acid (E)], [6% EDA, 7.5% orthophosphoric acid (F)].

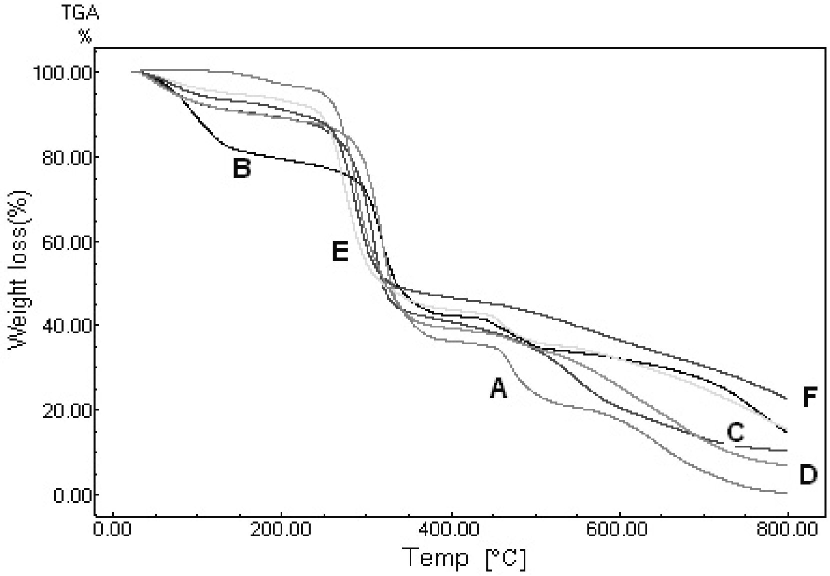

Figure 9. TGA Thermographs of: original PVC membrane (A), [6% EDA, and 1.5% orthophosphoric acids (B)], [6% EDA, and 3% orthophosphoric acid (C)], [6% EDA, 4.5% orthophosphoric acid (D)], [6% EDA, 6% orthophosphoric acid (E)], [6% EDA, 7.5% orthophosphoric acid (F)].

The values of weight loss percentage as function of original PVC, aminated and OPA doped membranes are listed in Table 3. Its clear from data tabulated that the weight loss percent for all aminated and OPA doped membranes is less than that of original PVC, which indicates that the modified membranes prepared in this work are more thermally stable than original PVC membranes.

Table 3. Weight loss percent at 500 °C of original, aminated and OPA doped PVC membranes

Concentration%	Weight loss %
Original PVC	80.00
6%EDA,1.5%orthophosphoric acid	65.00
6%EDA,3%orthophosphoric acid	61.00
6%EDA,4.5%orthophosphoric acid	55.00

3.6. Ion-exchange capacity (IEC)

Ion-exchange capacity (IEC) indicates the density of ionizable hydrophilic groups in the membrane matrix, which are responsible for the ionic conductivity of the membranes, and thus is an indirect approximation of the proton conductivity [24], which is one the main objectives of application the proton exchange membranes in direct methanol fuel cells. Table 4 displays the IEC for PVC and PVC-OPA doped membranes as determined from acid base titration method, in respect to the OPA concentration. For the comparison of the IEC for the original PVC membrane was determined by the same method and under the same conditions. IEC of the OPA doped membranes is greater than the IEC of original PVC and is linearly increases with increasing concentration of orthophosphoric acid.

Table 4. IEC for original PVC, aminated and PVC-OPA doped membranes

Orthophosphoric acid concentration (%)	IEC (meq/g)
0	0
1.5	2.50
3	2.90
4.5	3.25
6	3.43
7.5	3.41

4. CONCLUSIONS

Novel acid-base poly vinyl chloride- doped phosphoric acid membranes for fuel cells applications were prepared and characterized for the first time. Membranes were prepared by amination process using EDA followed by doping with orthophosphoric acid having (–PO3H) groups to the imide sites on the membranes. The later are significantly contributed to enhance thermal stability where weight loss at 500^{o}C reduced from 80% for original PVC to 55% for OPA doped membranes with 4.5% OPA. Ion exchange capacity improved to reach 3.43 (meq.g). Water uptake improved significantly to reach at maximum to 105%. The thickness of membranes increases with increase of orthophosphoric acid concentration. This makes the PVC-OPA doped membranes promising and attractive new material in application in fuel cells.

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