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# Synthesis and characterization of sulphonated poly (ether ether ketone)-phosphorized (zirconia) nano-composites as polymer electrolyte for fuel cell application

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## ABSTRACT

Polymer blends of Sulphonated Poly Ether Ether Ketone (SPEEK)/Phosphorized Zirconia (PZD) with varying concentrations of PZD, were considered as materials for synthesizing Polymer Electrolyte Membranes (PEM). The PZD was added to check for variations in the mechanical stability, solvent absorption and proton conductivity of the composites with virgin SPEEK. The membranes were cast from solution using N,Methyl-2-Pyrrolidone (NMP) as solvent. Preliminary lab results showed a decrease in Ion Exchange Capacity (IEC) for composites from virgin SPEEK, a decrease in the water and methanol absorption was evident in the composites. FTIR confirmed the presence of sulphonic acid groups in the membranes and XRay Diffraction (XRD) confirmed the amorphous nature of the composites. Scanning Electron Microscopy (SEM) showed good homogeneity of the composites without any phase separations. Thermal analysis confirmed thermal stability of the composites membranes upto 250°C and tensile test measurements showed higher tensile strength for the composites than virgin SPEEK. Electrochemical Impedance (EIS) showed an increase in proton conductivity for the composites when compared to virgin SPEEK. After characterization, Membrane Electrode Assembly (MEA) was fabricated with Nafion, SPEEK, SPEEK-PZD for performance evaluation of the membranes. The composites showed higher current density when compared to virgin SPEEK and Nafion.

## KEYWORDS

Sulphonated poly ether ether ketone (SPEEK);
Phosphorized zironia;
composites;
Phosphoric acid;
Polymer electrolyte Membrane fuel cell;
Membrane electrode assembly.

## INTRODUCTION

Nafion prevails as a reliable Proton Exchange Membrane (PEM) for fuel cells, considering its very good proton conductivity, water absorption, durability and dimensional stability[1]. However, in an era where sustainable growth and green technology is given crucial importance, Nafion, with its fluorine backbone can be a cause for a serious concern in terms of high cost, environmental factors, and poor-capability to perform at high operating temperatures[1,2]. It is vital to pursue research in the field of alternate PEMs for fuel cell applications, which can provide an undying solution to the environmental concerns, cost considerations and performance which is in commensuration or better than that of the prevalent Nafion membrane. Sulphonated Poly (Ether Ether Ketone) membranes have been investigated extensively[1-3] as alternatives for Nafion primarily due to the flexible ether ether linkage, good water absorption, moderate proton conductivity and ability to perform at temperatures upto 180°C[3,4], most importantly, SPEEK membranes are less expensive. An important consideration for PEM is its ability to withstand the corrosive environments in the fuel cell and good mechanical properties. This can be achieved by blending SPEEK with another polymeric material, which can effectively combine with SPEEK without any phase separation. Many works based on SPEEK with aromatic thermoplastics have resulted in membranes with good chemical resistance, high thermo-oxidative stability, mechanical strength. SPEEK-Polybenzimidazole (PBI) blends were synthesized in which increasing concentration of PBI in SPEEK showed improved tensile strength, thermal stability and decrease in methanol uptake[5]. SPEEK-PANI composite membranes showed reduced methanol uptake upto four times lower than Nafion 117 and reasonable electrochemical data and thermal properties[6].

The current research aims at developing alternative PEM using SPEEK-PZD composites and are synthesized and tested for the application as PEMs in PEMFC. Zirconia is phosphorized to improve proton conductivity. Furthermore, PZD tend to form strong interactions with SPEEK and mix homogenously without any phase separations[7]. SPEEK-PZD composite is expected to show better properties than virgin SPEEK in terms of tensile strength, initial decomposition temperature.

The objectives of the present work are

Synthesis of virgin SPEEK and SPEEK-PZD membranes

Testing of composites for IEC, solvent absorption and chemical stability

Characterization of composites using FT-IR, XRD, TGA, SEM, EIS, UTM

Fabrication of MEA and performance evaluation in PEMFC

## EXPERIMENTAL

### Materials and methods

### Sulphonation of PEEK

PEEK powder, 150XF, was purchased from Victrex, England. Sulphuric acid (AR) was purchased from Nice Chemicals. Zirconia was purchased from Sigma Aldrich and NMP, Analytical reagent, was purchased from Nice Chemicals, Ortho-Phosphoric Acid (AR) was purchased from Nice Chemicals. 10 g of PEEK powder was taken in a round bottom flask and reacted with calculated quantity of sulphuric acid for 6 hours[2,8]. The reaction was carried out at room temperature using a magnetic stirrer under constant rpm. The reaction was terminated at the end of six hours in an ice bath and resulting Sulphonated PEEK (SPEEK) fibres obtained were washed in double distilled water until the pH of the washwater is neutral.

### Synthesis of SPEEK and SPEEK-PZD composite membranes[7-9]

For the preparation of the membrane, the following procedure was adopted. SPEEK was dissolved in NMP at room temperature. The resulting solution is stirred for some time. The homogenous solution obtained is then filtered and cast onto a clean dry petri dish. Membranes were obtained by drying the contents of the petri dish at 60°C. The obtained membranes were pale brown in colour.

For phosphorization of Zirconia, few grams of Zirconia and Acetic acid with standard molarity were taken and stirred in magnetic stirrer and sonicated for some time to disperse Zirconia in acetic acid. 50 ml of 5% Phosphoric acid solution was added into $ZrO_2$ suspension to phosphorize $ZrO_2$. The mixture after being stirred was heated upto 90°C in an oven and allowed to cool

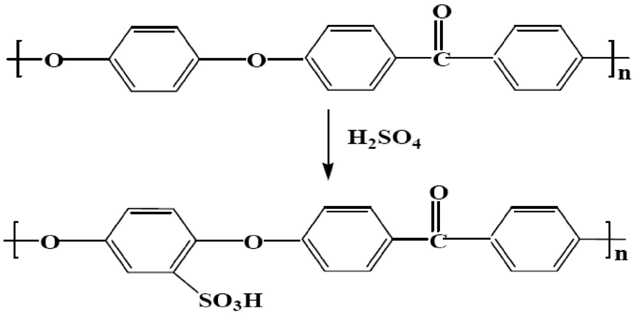

Figure 1 : Sulphonation of PEE

down to room temperature. Resultant precipitate (PZD) was filtered and dried.

For the composites, measured quantity of PZD was dispersed in NMP and the solution is stirred. The PZD solution was then added drop by drop into the SPEEK in NMP solution and the resulting mixture was stirred for a further 4 hours till it turned homogeneous[7,8]. This homogeneous solution was cast onto a clean petri dish and the contents were dried in the oven at 60° C for slow evaporation of the solvent to avoid any fissures in the final membrane. After the solvent had evaporated, the membranes were peeled off from the petri dish, treated with 0.5N $H_2SO_4$, and washed with deionized water. A set of five different composites with varying PZD concentrations of 2%, 4%, 6%, 8%, 10% were synthesized using the aforesaid technique. The synthesized membranes were of 80-100µ thickness.

## Fabrication of Membrane Electrode Assembly (MEA)[4,8]

The procedure for preparing a MEA adhered to standard protocols. Carbon Vulcan XC-72 was purchased from Precision Scientific, Coimbatore. Pt on Vulcan XC-72 was purchased from Arora Matthey. Teflon dispersion was purchased from Sigma Aldrich. Isopropyl Alcohol (IPA) was purchased from Rankem Chemicals.

## Purification of the membrane

Purification of the membrane is very crucial and must be performed before preparing the MEA. Initially, all membranes were allowed to boil in 3% $H_2O_2$ for 45 minutes. This removes the impurities, if any, present on the surface of the membrane. The membranes were then washed thoroughly with distilled water and boiled for 30 minutes in 10% $H_2SO_4$ to remove any inorganic impurities and to get the membrane in a complete protonated form. Finally, the membrane was washed with boiling water to remove any excess acid present on the surface of the membrane and dried.

## Teflonization of the porous carbon cloth

For the teflonization process, a 60% teflon dispersion in water available commercially was procured and was further diluted with deionised water in the ratio of 1:5. the carbon cloth is highly porous in nature and is dipped in the above dispersion for 15 seconds. then it is placed in a muffle furnace at 350°C for 5 hours. the process of teflonization improves the hydrophobicity of the carbon cloth.

## Carbonization of the teflonized carbon cloth

This is also called as the Gas Diffusion Layer (GDL). Initially Vulcan XC-72 (3mg/cm$^2$) was mixed with 3ml of deionised water and sonicated for 10 minutes. The sonication is done to obtain a fine dispersion of the carbon particles. Then 2-3 ml of isopropyl alcohol was added and sonicated again for 10 minutes. Finally, a drop of Teflon dispersion was added, mixed and immediately coated on the carbon cloth by means of a brush. The cloth was then kept in a muffle furnace at 350°C for 5 hours.

## Catalyst layer first stage coating

### Anode

The catalyst used is Pt dispersed in carbon. For the first stage, the amount of Pt taken was 0.125 mg/cm$^2$. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of IPA was added and sonicated for another 10 minutes. Finally, one drop of Teflon dispersion was added, mixed with the help of a painting brush and coated immediately on the carbonized cloth. It was then allowed in a muffle furnace at 350°C for 3 hours.

### Cathode

The catalyst used is Pt dispersed in carbon. For the first stage, the amount of Pt taken is 0.125 mg/cm$^2$. The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of IPA was added and sonicated for another 10 minutes. Finally, one drop of Teflon dispersion was added, mixed with the help of a painting brush and coated immediately on the carbonized cloth. It was then allowed in a muffle furnace at 350°C for 3 hours.

## Catalyst layer second stage coating

### Anode

The catalyst used is Pt dispersed in carbon. For the second stage, the amount of Pt taken was 0.125 mg/cm$^2$. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of S-PEEK solution is added and then coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It was then dried in a hot air oven at 80$^{o}$C for 4 hours. The electrode obtained after drying can be used as the anode for the fabrication of the MEA.

### Cathode

The catalyst used is Pt dispersed in carbon. For the second stage, the amount of Pt taken was 0.375 mg/cm$^2$. The required amount of the catalyst is weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of S-PEEK solution is added, mixed and coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It is dried in an oven at 80ÚC for 4 hours. The electrode obtained is the cathode that can be used for the fabrication of the MEA

### Hot pressing of the electrodes on the membrane

On either side of the membrane, a solution of SPEEK in NMP was applied and the electrodes were placed on either side. It was hot pressed at 80$^{o}$C for 45 seconds with a load of 0.5 tonnes. The two electrodes stuck onto the membrane after the hot pressing treatment. The resulting assembly is the Membrane Electrode Assembly.

### Fourier transform infrared spectroscopy (FTIR)

The IR spectra (450 – 4000 cm-1) for the dried membranes were recorded with a Perkin Elmer FT-IR spectrometer with an accuracy of ± 0.001 cm$^{-1}$ at 25 ± 2 ° C. The samples were dried at 100 ºC for an hour before recording the spectrum.

### X-Ray diffraction (XRD)

XRD measurements were performed using an X' Pert Pro diffractometer. The dried samples were mounted on an aluminium sample holder. The scanning angle ranged from 1° to 80° with a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2 ° C).

### Scanning electron microscopy (SEM)

The surface morphology of the electrolyte membranes were analysed using SEM (Hitachi S– 3400 N).The samples were cut into sufficient size and sputter coated with gold to make the samples electro conductive. The samples were then analyzed under vacuum condition at an accelerating voltage of 10 KV.

### Thermogravimetric analysis (TGA)

TGA analysis is mainly carried out to determine the thermal stability of the membranes. The change in weight of the membrane with increase in temperature at a heating rate of 10°C/min in the range of the temperature between 30°C and 500°C is followed using a STA 449 F1/F3 Jupiter analyzer. All the runs were carried out under nitrogen atmosphere.

### Universal testing machine (UTM)

The tensile testing is done according to ASTM D 638, (Type V) wherein the polymer samples are cut in dumbbell shape with specified dimensions. Hounsfield UTM was used for the purpose. The testing was done in standard laboratory atmosphere of 23°C ± 2°C and 50 ± 5 % relative humidity at a crosshead speed of 10 mm/min and 500 N force.

### Ion exchange capacity (IEC)[4,8]

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1g of the dry polymer. It was determined by titration method. The membrane in its protonated form was weighed and then soaked in an aqueous solution containing a large excess of KCl in order to extract all the protons from the membrane. The electrolyte solution was then neutralized using a very dilute $Na_2CO_3$ solution of known concentration (0.01N). The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and the normality of the $Na_2CO_3$ solution. The IEC values were expressed as number of meq. of sulphonic groups per gram of dry polymer.

IEC is calculated using the formula,

$$\text{IEC (meq/g)} = \frac{\text{Titer value (in ml) x Normality of Titrant}}{\text{Weight of the dry membrane (in grams)}}$$

### Solvent absorption[4,8]

The amount of solvent intake by the membranes was studied. The dried membranes were weighed and soaked in water and methanol separately and allowed to get equilibrated at room temperature for 45 hours, above which the weight was constant. The swollen membranes were then quickly weighed after blotting the surface water and the values noted. The swelling degree was determined using the formula,

$$SA = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (\%)$$

where,
$M_{wet}$ = Weight of wet membrane,
$M_{dry}$ = Weight of dry membrane.

### Durability of membranes[8]

For checking the durability of the electrolyte membranes, the following procedure was adopted. Initially a 4ppm ferrous ammonium sulfate in 3% $H_2O_2$ was freshly prepared and the temperature of the solution was maintained at 80°C. The electrolyte membrane with the dimension of $0.5cm^2$was cut and soaked in the solution. The time required for the physical disintegration of the membrane noted down and reported. The reaction is expected to occur by free radical mechanism.

### Electrochemical Impedance Spectroscopy (EIS)

The proton conductivity measurements were taken using an alternating current impedance spectroscopy device over a frequency range of 1-107hz with 50-500mV oscillating voltage using a solatron gain phase analyzer. Films having 13mm diameter, sandwiched between two stainless steel block electrodes with〈 “3 kg/cm2 pressure, were placed in an open, temperature-controlled cell. The films were previously hydrated by immersion for 24 h at room temperature. The conductivity $\sigma$ of samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = d/RS$, where $d$ and $S$ are the thickness and face area of the membrane sample, respectively, and where *W*as derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the Re($Z$) axis. The impedance data were corrected for the contribution from empty and short-circuited cell.

### Performance evaluation

All the samples were subjected to testing in real time PEMFC environment with hydrogen gas as fuel. Standard bipolar plates and copper current collectors were used for this purpose. A multimeter was used to detect the current for each load set by the load box. Operating conditions were room temperature and atmospheric pressure.

## RESULTS AND DISCUSSIONS

### FTIR

Figure 2 shows the comparative FTIR spectra of SPEEK and the various compositions of SPEEK-PZD composites. All the six spectra exhibit an absorption peak at approximately 1580 $cm^{-1}$[9]as a result of C=C stretching and an absorption peak at 1680 $cm^{-1}$ owing to the C=O stretching. The characteristic stretch for O=S=O group is in the region of 1050 $cm^{-1}$[9]. The experimental values coincide with the data from literature [9] as the peaks for SPEEK at 1077$cm^{-1}$ and 1021 $cm^{-1}$ confirm the presence of O=S=O groups. Similarly, the blends of 2% PZD show stretching at 1075 $cm^{-1}$ and 1018 $cm^{-1}$confirming sulphonation. The 4% PZD, 6% PZD, 8% PZD, 10% PZD composites showed similar stretching at 1080 $cm^{-1}$ and 1022 $cm^{-1}$, all of which corroborate the sulphonation of the polymers.

Figure 3 shows the comparative FTIR spectra of Zirconia and Phosphorized Zirconia. Phosphorization occurred at 1047 $cm^{-1}$

### XRD

From the Figure 4, we find that the intensity of the peak decreases from SPEEK to the composites. If the intensity of peak is greater, then the crystalline nature is greater in the sample. We can conclude that as the concentration of PZD increases, the amorphous nature of the membrane also increases. Amorphous compounds have their atoms separated wide apart providing excellent mechanical strength and durability to the mem-

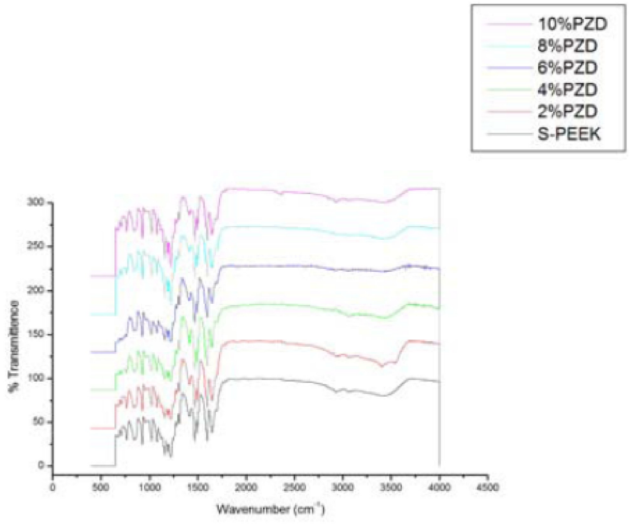

Figure 2: FTIR of SPEEK and SPEEK-PZD Composites

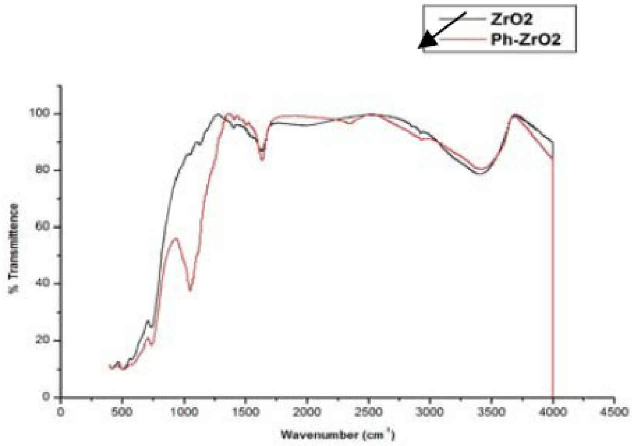

**Figure 3 : Shows the comparative FTIR spectra of Zirconia and Phosphorized Zirconia. Phosphorization occurred at 1047 cm$^{-1}$**

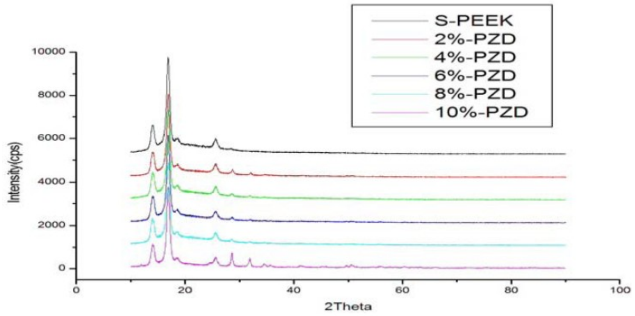

**Figure 4: XRD patterns of SPEEK and SPEEK-PZD composites**

branes. The SPEEK-PZD membranes thus potentially possess higher mechanical properties due to its increased amorphous nature.

The SEM images of SPEEK and a representative composite membrane are given in Figure 5. They look dense, clear and homogenous (absence of phase separation) indicating a very good compatibility between the constituents. Even at higher magnifications, the blend membranes showed no fissures, which may be due to the use of high boiling solvent for the casting purpose. The evaporation of NMP solvent (boiling point 202°C) was performed at 80°C indicating a very slow process of evaporation.

## TGA

The thermogram of SPEEK and various composites are given in Figure 6. A more careful evaluation of the thermogram of the composite membrane revealed a trend similar to SPEEK. A three-stage decomposition is observed for the composite membranes. The first weight loss is observed between 70°C and 125°C. This could be due to the loss of physically and chemically adsorbed water. This loss is minimum for the composite membrane with 10% PZD and maximum for 2% PZD. When the concentration of PZD is increased in the composites, it results in a lower absorption of water[7]. The second loss observed between 230°C and 460°C could be due to the splitting of the sulphonic acid groupings. The final weight loss above 500ÚC could be due to the decomposition of the polymer backbone.

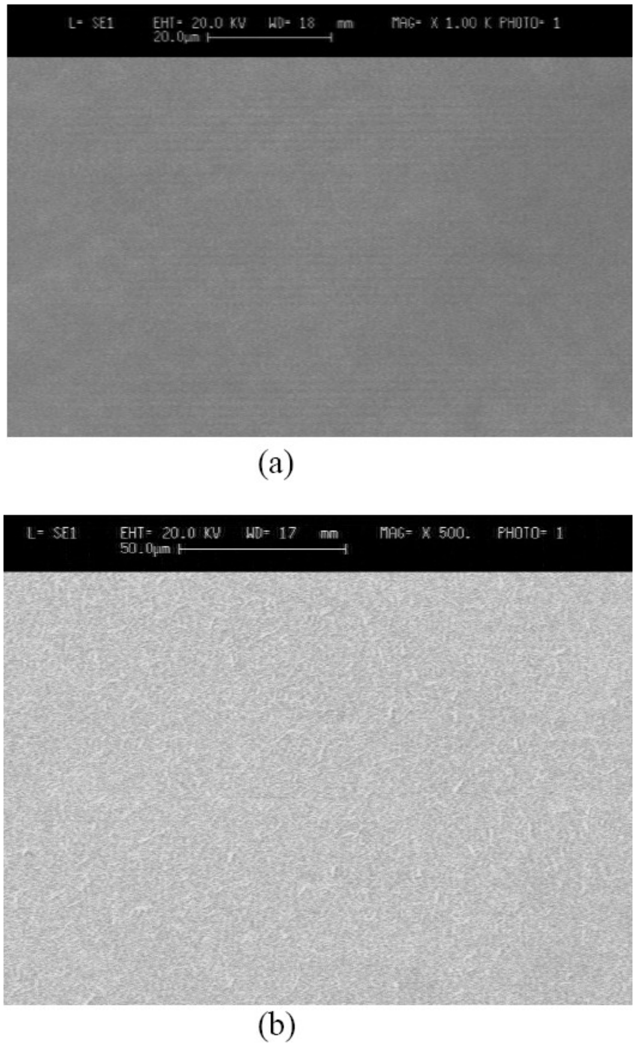

**Figure 5 : SEM images of (a) virgin SPEEK membrane and (b) SPEEK-10%PZD**

The results of tensile strength and percentage elongation at break of SPEEK and the composite membranes are given in Figure 7. As the two polymers are compatible with each other, an increase in the tensile strength is observed with increasing content of PZD, thus making the membrane stiffer. On the other hand, the percentage elongation decreases with increasing

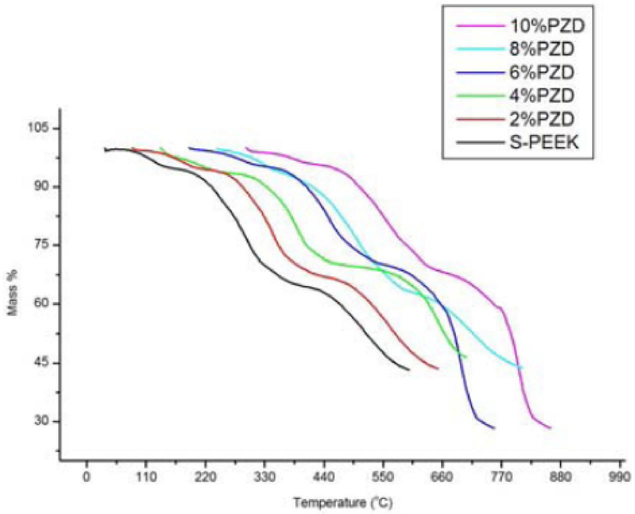

**Figure 6 : Thermogram of SPEEK and Composite Membranes**

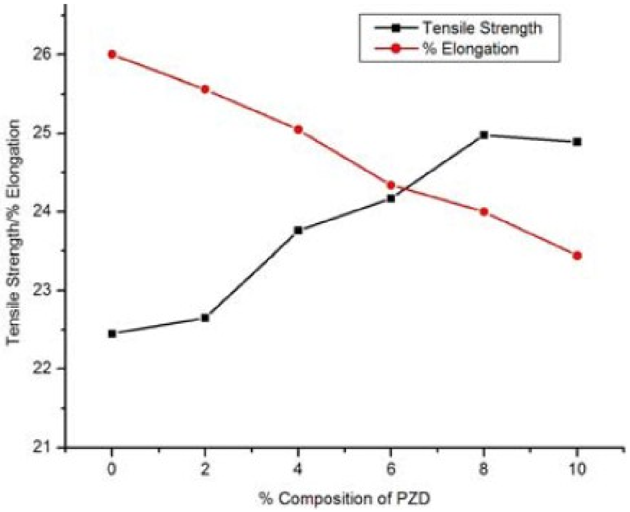

**Figure 7 : Percentage elongation and tensile strength of SPEEK and composites**

content of PZD. The membranes are getting more and more stiffer with the addition of PZD, the membranes resist to elongate much and hence break without much elongation.

## Ion exchange capacity (IEC)

The results from the measurements of IEC values for SPEEK and composite membranes are shown in Figure 8. In order to explain the trends seen in Figure 8, the presence and amount of available $H^+$ ions in sulphonic acid groups that directly influence the conductivity of the membranes is noted. As the composition of PZD in the composite increases respectively, there is a decrease in the number of effective replaceable protons. The effective amount of SPEEK decreases, with an increase in the content of PZD in the case of composites.

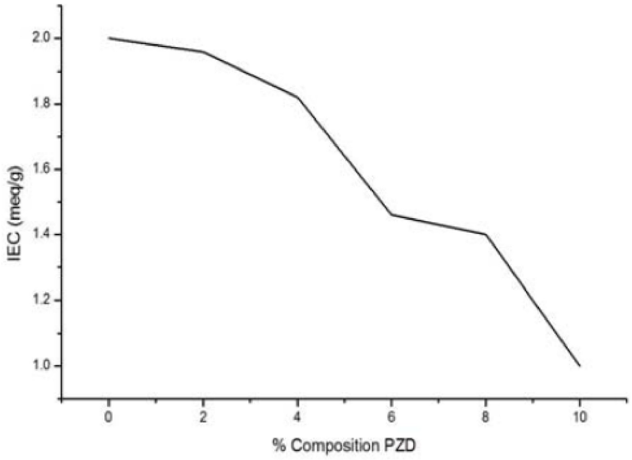

**Figure 8 : IEC of SPEEK and Composites**

## Solvent absorption

The solvent absorption results for SPEEK and various composite membranes are shown in Figure 9. Water and Methanol, both polar in nature, were the two solvents used in this aspect of the product characterization. It is known from the prior work reported in the literature[9] that increased water uptake leads to increase in the conductivity of the membrane. However, beyond a threshold (>30% to 40%), the benefit of increased conductivity is offset by the onset of mechanical degradation of the membrane.

On comparing the water uptake of Nafion®117, which is known to be 38%[10], the composite membranes (with PZD) show a value of approximately 30% to 40%. An increase in the percentage of PZD in composites is seen to cause a decrease in the water and methanol uptake. This can be explained by the fact that hydrophilic $SO_3H$ groups decrease on addition of PZD.

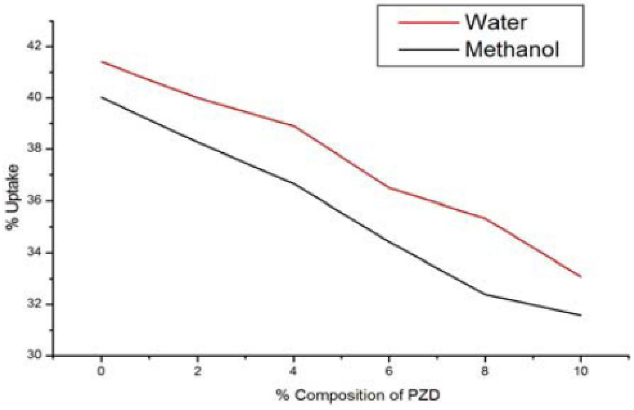

**Figure 9 : Solvent absorption of SPEEK and composite membranes**

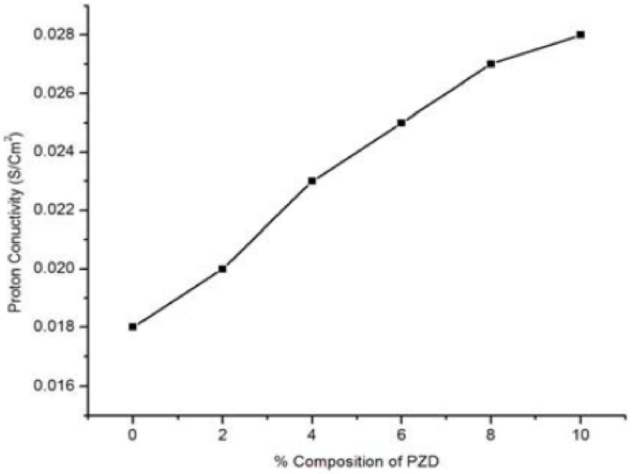

**Figure 10: Proton conductivity SPEEK-PZD Composites**

Though the graph shows a decreasing trend in Water and Methanol uptake, membranes still exhibit optimum water retention property necessary for proton conduction.

## Durability studies

The time required for the degradation of SPEEK and composite membranes are given in TABLE 1. Chemical and mechanical degradation expectedly have an adverse effect on the durability of the membrane. The stability studies of the membrane towards peroxide solutions give an idea about the lifetime (durability of membrane) of the membrane. The peroxide test is considered as an accelerated stability testing method. In the present study, the durability of the composite membranes showed a constant value with increasing concentration of PZD. This is a favourable trend for applications in electrochemical devices. Virgin SPEEK withstood the test condition for 3 hours. All the composite membranes exhibited a comparable stability in Fentons reagent at 80°C indicating that the stability of the composite membrane are comparable to the stability of SPEEK.

**TABLE 1 : Durability of SPEEK membranes with PZD composites**

| Membrane | Time for Disintegration |
|---|---|
| S-PEEK | 3 hours |
| 2% PVP | 3 hours 15 minutes |
| 4% PVP | 3 hours 15 minutes |
| 6% PVP | 3 hours 30 minutes |
| 8%PVP | 3 hours 30 minutes |
| 10% PVP | 4 hours |

## Proton conductivity

The results of the proton conductivity of SPEEK and composites are given in Figure 10. As the amount of PZD increases, the number of exchangeable $H^+$ ions ($SO_3H$ groups) decreases in the sample. This inhibits proton transport across the membrane thereby decreasing the effective proton conductivity. However, an important aspect to note here is the capability of PZD to improve proton conduction. Acidic modification (Phosphorization) of Zirconia supplements proton conductivity of the membranes. Hence, even though the amount of $SO_3H$ groups decreases with increasing PZD, the proton conductivity increases.

## Performance evaluation

The current obtained at various loads for SPEEK and composite membranes are given in Figure 11. SPEEK-PZD composites posses the potential of performing equivalent to or better than Nafion in a PEMFC environment. Moreover the voltage measured for increasing composition of PZD composite membranes are better than that of Nafion. This can be attributed to the fact that Proton conductivity improves due to the addition of phosphorized Zirconia.

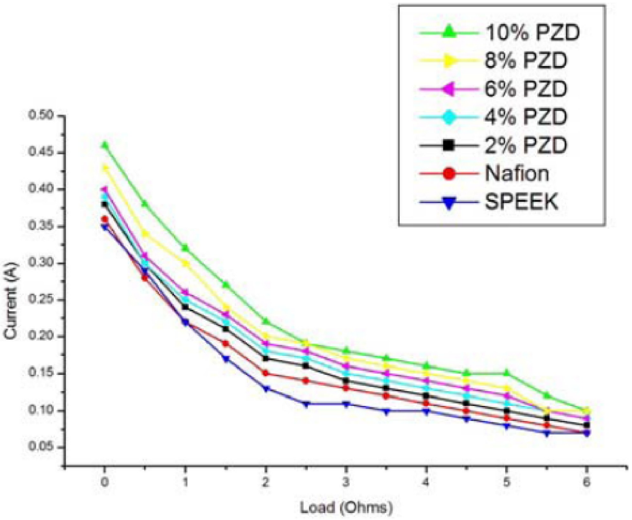

**Figure 11 : Performance plots**

## CONCLUSIONS

From the results documented, we can conclude that SPEEK- PZD composites are good candidates for PEM Fuel Cells owing to their high stability in corrosive environments, improved proton conductivity, good thermal stability and mechanical properties. The membranes can also be used for DMFCs due to low methanol absorption.

## ACKNOWLEDGMENT

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