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# Electrochemistry

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## Organic/inorganic composite membranes for proton exchange membrane fuel cells

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### ABSTRACT

A flexible composite membrane with homogeneously distributed zirconia and titania was prepared using sulphonated polystyrene ethylene butylene polystyrene (SPSEBS) and commercial zirconia and titania. The composite membranes of SPSEBS up to 10 wt% zirconium dioxide and titanium dioxide content were prepared. The study was oriented towards the optimization of the synthesis and characterization of such composite membranes to choose the best inorganic composition in terms of thermal stability and proton conductivity. The proton conductivity of the composite membrane was measured using electrochemical impedance spectroscopy (EIS). The thermogravimetric analysis (TGA) analysis of the composite membranes showed better thermal stability than SPSEBS membrane and at the same time, higher content (wt.%) of inorganic material decreased the proton conductivity. A good adhesion between inorganic domains and the polymer matrix was confirmed through morphology studies such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). The methanol permeability and selectivity ratio were decreased with increasing inorganic materials. The feasibility of these hybrid membranes as proton conducting electrolyte in proton exchange membrane fuel cell (PEMFC) was investigated and results were compared with that of commercial Nafion 117 membrane. The single fuel cell test showed that the fuel cell with homogeneous composite membrane showed better performance under the fuel cell operating condition.

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### KEYWORDS

Titania composite;  
Zirconia composite;  
Fuel cells;  
SPSEBS;  
PEMFC.

### INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) show excellent performance, providing the right composition and operating conditions. The PEM plays an important role in the development of the fuel cell tech-

nology. In particular, it should exhibit high proton conductivity, along with long-term mechanical stability<sup>[1]</sup>. The three main characteristics considered by the standard characterization methods are,

- **Proton conductivity:** It gives an estimate of the proton conductivity, which is the main function of a

proton exchange membrane. This property is usually evaluated with acid or water electrolytes (hydrated membranes) by impedance spectroscopy<sup>[2]</sup>.

- **Permeability to methanol:** The methanol mass transport through DMFC membranes is very common which results in detrimental effect on the DMFC performance<sup>[3]</sup>.
- **Water swelling:** It is usually associated with improved proton conductivity<sup>[4]</sup>.

However, current PEMFCs still suffered from the severe conditions, for example, low humidity, high temperature and excessive gas contaminants. The challenge for the PEMFCs as a new power source is that they must operate over a wide range of conditions and meet stringent cost requirements. Particularly, it is desirable for portable applications that the fuel cells operate without external humidification. Nanoscaled SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub> and heteropolyacids are the common inorganic materials used for producing such composite membranes for PEMFCs<sup>[5-8]</sup>.

The present study aims at expanding the characterization of a series of organic–inorganic composite membranes with an extended range of zirconium dioxide and titanium dioxide contents (1–10 wt.%), from standard characterization methods to test under PEMFC conditions.

Currently the major developments in fuel cell technology using hydrogen or methanol are based on perfluorinated and sulphonated solid polymer electrolytes. These solid electrolytes offer advantages over classical liquid electrolytes such as sulphuric acid. These advantages include reduced methanol crossover and higher power densities. Sulphonic acid insertion into solid polymer membrane is currently employed and is commercially referred to as Nafion. This membrane is very popular when used as a low temperature proton conducting polymer membrane. This membrane is a good proton conductor and is the preferred membrane for both hydrogen and direct methanol fuel cells (DMFC)<sup>[9]</sup>.

Nafion is very expensive and has a negative influence on pricing resulting in high cost fuel cells not affordable to the public. (i) Most membranes currently used in PEMFCs and DMFCs were not designed to operate at high temperatures where high temperature fuel cells have the ability to reform some hydrocarbon fuels directly, (ii) The high methanol permeability through

the membrane resulting in catalyst poisoning and reduced cell potential, (iii) Low temperature designed membranes such as Nafion dehydrates as the temperature nears and exceeds 100 °C. There are several reasons for the development of new membranes, (i) operation of PEMFC at above 140 °C temperatures receiving worldwide attention (ii) consideration of the environmental friendliness of materials (iii) reduction of membrane cost<sup>[10-12]</sup>.

This paper reports the influence of zirconia and titania on proton conductivity and thermal stability of sulphonated polystyrene ethylene butylene polystyrene/ zirconia and titania composite membranes. The selection of SPSEBS as polymer matrix is due to its high thermal strength, cheapness, easy handling ability, low methanol crossover and good proton conductivity.

## EXPERIMENTAL

### Materials and methods

Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene (PSEBS) (Mw = 89,000; 29% styrene) was obtained from Aldrich (Germany). Chlorosulphonic acid (CSA) was purchased from Spectro-Chem, India and used without further purification. Tri - butyl phosphate (TBP) (Lancaster) and methanol (SRL) were purchased and used as received. The tetrahydro furan (THF) solvent was purchased from Merck. Titania (10-15 nm; CAS no. 13463-67-7) and zirconia (10-15 nm; CAS no.1314-23-4) with high purity of 99% each, were purchased from Sigma Aldrich (USA).

### Sulphonation of PSEBS

The PSEBS was dissolved in a measured quantity of chloroform to get a clear polymer solution and the solution was allowed to cool in an ice bath. Then a required amount of chlorosulphonic acid (CSA) was added drop wise over a period of time with constant stirring. The reaction was carried out for three hours and was terminated by adding methanol. The sulphonated PSEBS was recovered after removing all the solvent by evaporation. The product was washed with DI for several times until a neutral pH was obtained. The product was then dried at 75 °C for 24 hrs.

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### ZrO<sub>2</sub> and TiO<sub>2</sub> composite membrane preparation

Sulphonated PSEBS (SPSEBS) and silica were dissolved in THF solvent and five different weight percentages of ZrO<sub>2</sub> and TiO<sub>2</sub> (1, 2, 5, 7.5 and 10 wt %) having good dispersion in the same solvent also obtained separately. Then, the polymer solution was added to the ZrO<sub>2</sub> and TiO<sub>2</sub> dispersion and stirred until homogeneous solution was obtained. Finally, the entire system was cast on a glass plate and the composite membranes were obtained after 48 hours on evaporation of the solvent at room temperature. The resultant membrane was washed several times with deionized water and dried at 50 °C for 24 hours. The thickness of a dry membrane was about 200 ± 15 microns.

### Degree of sulphonation

The degree of sulphonation was calculated from the elemental analysis result. According to the literature method<sup>[13]</sup>, the elemental analysis was carried out for the sulphonated polymers to calculate the sulphonation degree. From the sulphur content, the degree of sulphonation was calculated according to the following equation.

$$DS = \frac{S_E \times 100}{S_T} \quad (1)$$

Where, S<sub>E</sub> and S<sub>T</sub> represent experimental and theoretical (assuming one -SO<sub>3</sub>H per repeat unit of SPSEBS) sulfur content of SPSEBS.

### Ion exchange capacity (IEC)

Ion exchange capacity is directly dependent on the number of sulphonic acid groups present in the sulphonated polymer. The sulphonated membranes and composite membranes were soaked in the 2M KCl solution for 24 hours to saturate the membranes and the protons released by the membranes were neutralized by sodium carbonate solution of known concentration with phenolphthalein as indicator. The IEC was calculated by using the equation

$$IEC = \frac{\text{Titer value (in ml)} \times \text{Normality of titrant (Na}_2\text{CO}_3)}{\text{Weight of the dry polymer membrane (in g)}} \text{ meq/g} \quad (2)$$

### Water absorption

Water uptake was measured according to the method described elsewhere<sup>[14]</sup>. Water uptake was

measured by immersing a sample sheet into water at room temperature. Then the membrane was taken out, wiped with tissue paper very quickly, and weighed on a microbalance. Water uptake was calculated from

$$\% \text{ swelling} = \frac{\text{Weight of the wet polymer} - \text{Weight of the dry polymer}}{\text{Weight of the dry polymer}} \times 100 \quad (3)$$

### Instrumentation

Thermal stability was analyzed using a thermo balance SDT Q600 US analyzer at a heating rate of 20 °C/min under nitrogen atmosphere. The glass transition temperature was obtained by differential scanning calorimeter.

The measurement of mechanical properties was carried out by HOUNSFIELD universal testing machine. The tensile strength of the membranes was determined at ambient condition. The samples were carefully cut in to a size of 5 x 50 mm, the cross head speed was set at 10 mm/min and up to failure of the material.

The membrane morphology can be investigated by scanning electron microscope with energy disperse spectrometer. Composite membranes were scanned for their morphology to check the uniform dispersion of the inorganic material in the polymer matrix using the AFM technique using micro fabricated silicon cantilevers with a force constant of approximately 40 N/m.

To know the level of dispersion of the inorganic content in the polymer membranes and to know the amount of crystallinity, XRD measurements were performed using a X'pert pro Diffractometer.

The conductivities of the membranes were determined by AC impedance spectroscopy. The measurements were taken using Volta lab dynamic-EIS voltammetry model PGZ 301.

### Membrane electrode assembly (MEA)

The electrodes for the single cell test in the FC consisted of gas diffusion and catalyst layers; the details of the electrode preparation are available elsewhere<sup>[15]</sup>. The fuel cell tests were performed on an Electrochem test bench using a 25 cm<sup>2</sup> active area single cell.

## RESULTS AND DISCUSSION

### Absorption studies

The water absorption values are shown in Figure

1. Water absorption of the membranes is usually defined in weight percentage with respect to the weight of the dry membrane. The absorption of water depends on the IEC. Higher the IEC, greater the absorption of the solvent. Initially the membrane rapidly absorbs the water and then gradually increases with time.

In the case of composite membranes, the water absorption increased with the increase in inorganic content. Two different composite membranes followed the same trend. This is shown in the Figure 1. The hydrophilic channels are responsible for such high absorption values. This leads to an overall swelling of the membranes. The greater swelling may be generated especially in the interface between polymer and inorganic material.

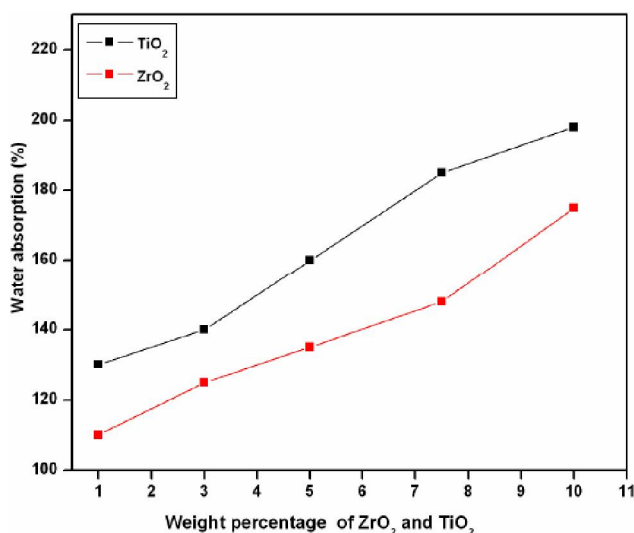


Figure 1 : Water absorption of SPSEBS/TiO<sub>2</sub> and SPSEBS/ZrO<sub>2</sub> composite membranes.

### Ion exchange capacity (IEC)

IEC provides an indication of the concentration of the number density of sulfonic acid groups present in the polymer matrix, which are responsible for the conduction of protons and thus is an indirect and reliable approximation of proton conductivity. It was observed that, as the concentration of the reinforcing materials increased, the IEC decreased. This is because of the incorporation of inorganic material in the polymer system. The values are shown in the TABLE 1.

### Thermal stability

The thermal analysis has been performed to investigate the patterns of dehydration. The thermogram of

SPSEBS/ZrO<sub>2</sub> composite membrane is shown in Figure 2A. There was a shift in peak maximum due to loss of SO<sub>3</sub>H group to higher value. Hence there might be enhanced polarization in SO<sub>3</sub>H group by ZrO<sub>2</sub>, thus enhancing its thermal stability. Once these groups have lost, the remaining polymer matrix decomposed at higher temperature, almost close to that of pure SPSEBS. So this observation suggests loss of SO<sub>3</sub>H group might not affect significantly the bonding properties of the remaining polymer matrix<sup>[16]</sup>.

TABLE 1 : IEC values with respect to the inorganic material content in S-PSEBS.

Membrane	IEC (meq/g)	Membrane	IEC (meq/g)
SPSEBS	2.07	SPSEBS	2.07
ZrO <sub>2</sub> - 1%	2.00	TiO <sub>2</sub> - 1%	1.94
ZrO <sub>2</sub> - 2.5%	1.95	TiO <sub>2</sub> - 2.5%	1.85
ZrO <sub>2</sub> - 5%	1.89	TiO <sub>2</sub> - 5%	1.76
ZrO <sub>2</sub> - 7.5%	1.84	TiO <sub>2</sub> - 7.5%	1.73
ZrO <sub>2</sub> - 10%	1.79	TiO <sub>2</sub> - 10%	1.72

The thermogram of SPSEBS/TiO<sub>2</sub> composite membranes is shown in Figure 2B. The trace is almost similar to that of pure SPSEBS. Hence TiO<sub>2</sub> might not be altering the bonding properties of the polymer matrix, but there was a shift in peak maximum due to loss of SO<sub>3</sub>H group to higher value. Hence there might be enhanced polarization in SO<sub>3</sub>H group by TiO<sub>2</sub>, thus enhancing its thermal stability. Once these groups were lost, the remaining polymer matrix decomposed at higher temperature, almost close to that of pure SPSEBS. So this observation suggests loss of SO<sub>3</sub>H group might not affect significantly the bonding properties of the remaining polymer matrix. If TiO<sub>2</sub> makes interaction with the polymer matrix, even after the decomposition of SO<sub>3</sub>H groups, there might be abrupt changes in the TGA trace. But the decomposition appears almost similar to pure SPSEBS, though the peak maximum was shifted to lower value, hence the decomposition of the polymer might not be influenced by TiO<sub>2</sub>. From the above discussion, it is concluded that TiO<sub>2</sub> supported SPSEBS would be conveniently applied for ion exchange applications even up to 225 °C.

### Differential scanning calorimetry

The DSC curves of SPSEBS- ZrO<sub>2</sub> and SPSEBS - TiO<sub>2</sub> are shown in the Figure 3. TiO<sub>2</sub> and ZrO<sub>2</sub> com-

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posites also showed two stage Tg temperatures. The first step Tg value around 160 °C for SPSEBS/TiO<sub>2</sub> composite and 200 °C for SPSEBS/ZrO<sub>2</sub> composite was mainly due to the sulphonated polymers and second transition was due to the inorganic material. The presence of inorganic material increased the Tg of composite membranes. This data reveals that, these inorganic materials are not bonded chemically with the polymer, although they are physically present in the matrix and still increased the glass transition temperature of the polymer. It also confirmed the suitability of the incorporation of the inorganic material in the polymer matrix.

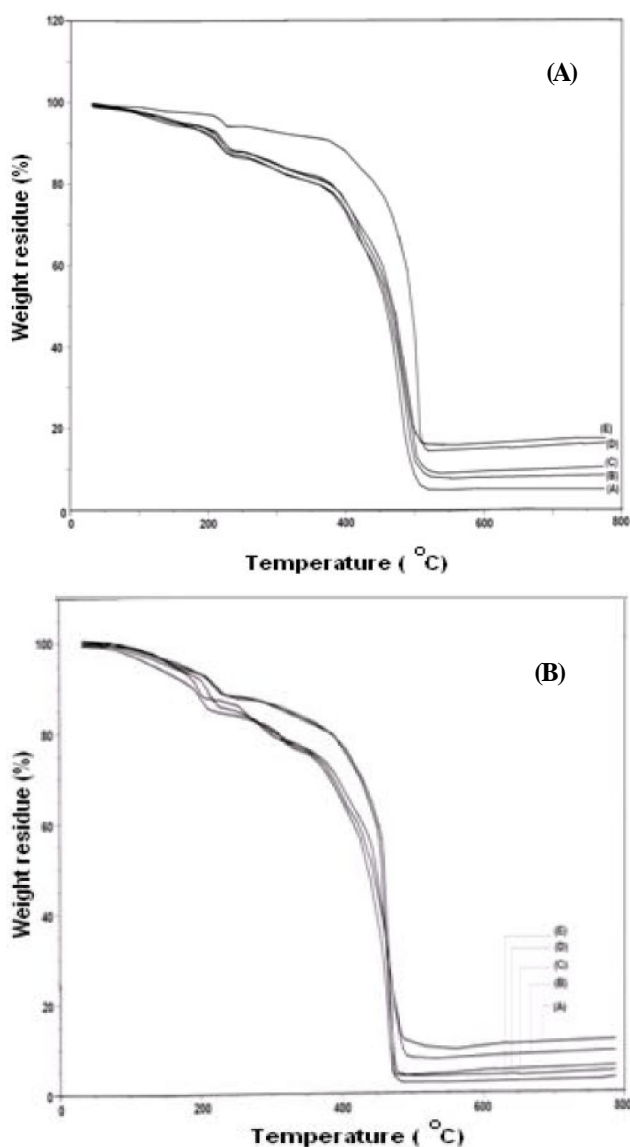


Figure 2 : TGA curves of (A) SPSEBS/ZrO<sub>2</sub> and (B) SPSEBS/TiO<sub>2</sub> composite membranes of 1, 2, 5, 7.5 and 10% of zirconia and titania content.

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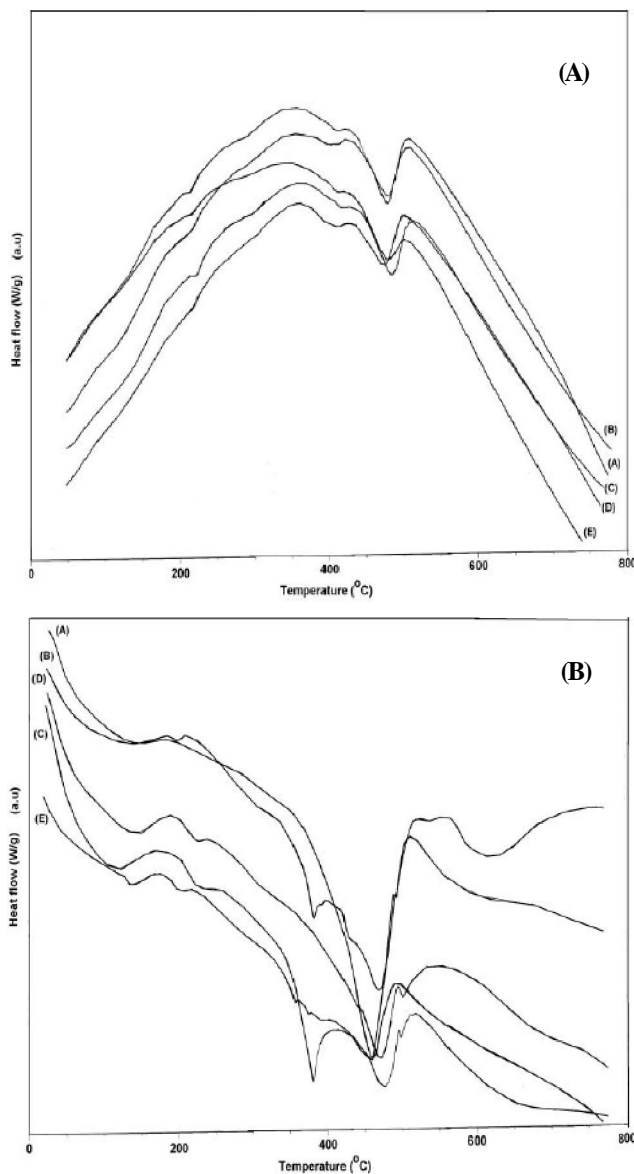


Figure 3 : DSC curves of (A) SPSEBS/ZrO<sub>2</sub> and (B) SPSEBS/TiO<sub>2</sub> composite membranes of 1, 2, 5, 7.5 and 10% of zirconia and titania content.

### AFM analysis

The cross section surface AFM images of the SPSEBS membrane and composite membranes are shown in the Figure 4. The area of the image is 5µm x 5µm in the x, y plane with an extended z axis. However, the surface was dramatically changed in inorganic incorporated membranes. The inorganic molecules affect the surface morphology of the membranes.

### X-ray diffraction studies

The XRD patterns of SPSEBS/ZrO<sub>2</sub> composite membranes are shown in Figure 5. The spectrum car-

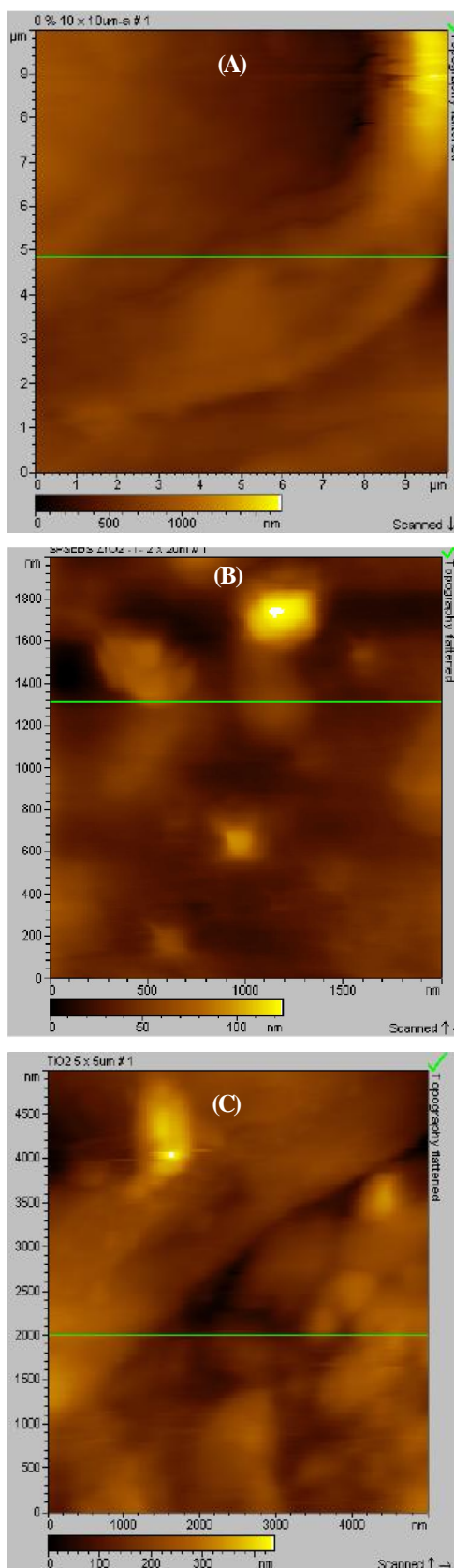


Figure 4 : AFM images of (A) SPSEBS (B)  $ZrO_2$  (5%) and (C)  $TiO_2$  (5%) composite membranes.

ries the patterns due to crystalline phase of SPSEBS and that of  $ZrO_2$ . But all the peaks of  $ZrO_2$  were not observed in the spectrum. It was verified by the comparison with XRD patterns of  $ZrO_2$  shown in Figure 5A. Some of the intense patterns of  $ZrO_2$ , for example, the peak at  $25.32^\circ$  ( $2\theta$ ) in Figure 5A, was completely absent in the spectrum. Though the other patterns were appearing, selective missing of this pattern illustrates strong interaction of the plane corresponding to this pattern of  $ZrO_2$  with the polymer matrix. This interaction keeps close to more of the polymer portion to this plane. Hence the diffracted rays from this plane might be completely false scattered by the polymer matrix. This observation also suggested both polymer and  $ZrO_2$  were not completely non interacting independent entities. This interaction might be the cause for shifting of a peak maximum corresponding to the decomposition of sulphonic groups of SPSEBS to higher values, as discussed in TGA analysis. Similar results were obtained for the  $TiO_2$  system shown in Figure 6.

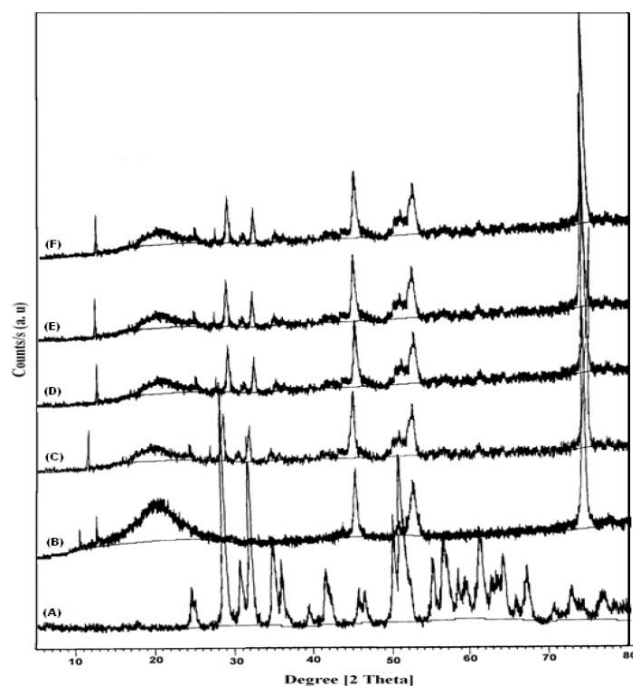


Figure 5 : XRD patterns of (A) zirconia and (B) to (F) SPSEBS/ $ZrO_2$  composite membranes of 1, 2, 5, 7.5 and 10% of zirconia content.

As enhanced crystallization of SPSEBS blocks more of the sulphonic acid groups in the crystal lattice, they might be expected to have slightly decreased conductivity and ion exchange properties.

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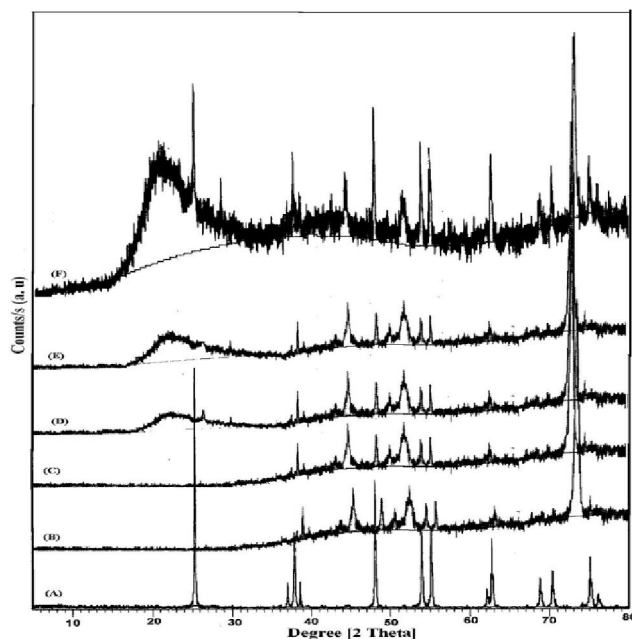


Figure 6 : XRD patterns of (A) titania and (B) to (F) SPSEBS/TiO<sub>2</sub> composite membranes of 1, 2, 5, 7.5 and 10% of titania content.

### Impedance spectroscopy

IEC provides an indication of the content of acid groups present in a polymer matrix, which are responsible for the conduction of protons and thus is an indirect and reliable approximation of the proton conductivity. Generally as the inorganic content increased, the proton conductivity decreases. The proton conductivities of SPSEBS membrane and composites were in the range of  $10^{-3}$  S/cm.

It can be also observed that the proton conductivity decreased with increase in the inorganic content as shown in Figure 7. It is believed that the in situ growth of the inorganic oxide phase in the polymer template was influenced by the nature of their functional groups. Thus in the case of SPSEBS polymer composite membranes, it can be assumed that during the membrane casting the inorganic particles occupy space between the molecules and decreased the hydrophilicity of the sulfonated polymer composite membranes. Consequently the water sorption capacity will be smaller, leading to a decrease in the proton conductance assisted by water dynamics.

### Single cell performance

Membranes developed based on titania and zirconia were self-humidifying composite membranes. The

membranes were fabricated from the high dispersion of metal oxides in a thin SPSEBS matrix. Membranes fabricated based on this concept should not require external humidification and should suppress the cross-over of H<sub>2</sub> and O<sub>2</sub>.

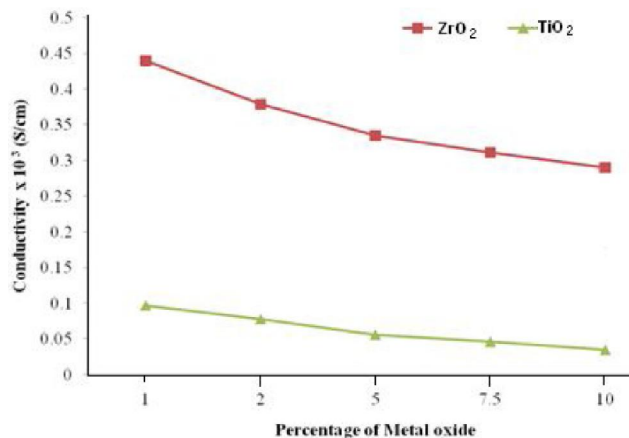


Figure 7 : Relationship between the proton conductivity and SPSEBS/metal oxide with various compositions.

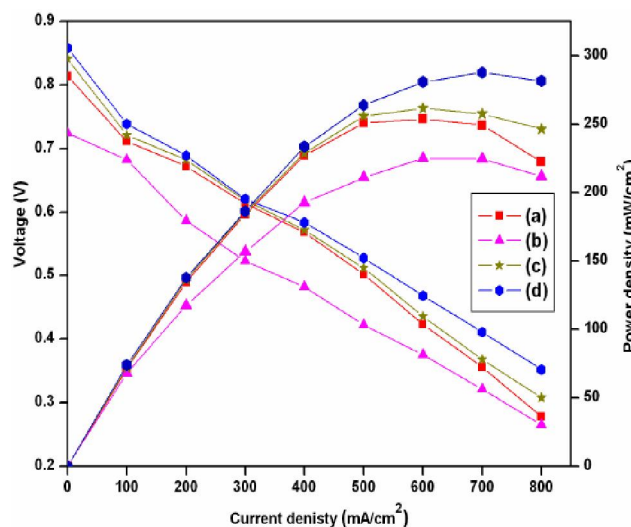


Figure 8 : Polarization curves for (a) SPSEBS, (b) Nafion 117, (c) SPSEBS/ZiO<sub>2</sub> (5%) and (d) SPSEBS/TiO<sub>2</sub> (5%) composite membrane at ambient temperature and H<sub>2</sub> and O<sub>2</sub> flow rates of 40 ml/min each.

PEMFC single cell (cell area = 25 cm<sup>2</sup>) performance of SPSEBS composite membranes with 5% metal oxide content were shown in Figure 8. Titania and zirconia composite membrane showed the OCP value of 0.858 V and 0.841 V respectively. The pristine SPSEBS membrane showed higher OCP value (0.814 V) compared to Nafion membrane (0.724 V). Maximum power density was achieved in the case of titania composite membrane (287.7 mW/cm<sup>2</sup>) com-

pared with zirconia composite membrane (261.6 mW/cm<sup>2</sup>), pristine SPSEBS (253.8 mW/cm<sup>2</sup>) membrane and commercially available Nafion 117 (225 mW/cm<sup>2</sup>) membrane.

The study demonstrated that composite membranes based on SPSEBS with TiO<sub>2</sub> and ZrO<sub>2</sub> could prove to be a viable strategy to overcome the difficulties of the currently used Nafion 117 membrane.

## CONCLUSION

The present study deals with the preparation of inorganic composite membranes using sulphonated-poly-styrene-ethylene-butylene-styrene and the inorganic reinforcement ZrO<sub>2</sub> and TiO<sub>2</sub> with various compositions. SPSEBS was synthesized by sulphonating the PSEBS using CSA as the sulphonating agent. The SPSEBS membrane and composite membranes were prepared by solution casting method. SPSEBS/metal oxide composites showed improvement in its mechanical and chemical stabilities. Hydrophilic nature of the metal oxides improved the solvent absorption characteristics. When the membranes were pressed at various temperatures, solvent sorption decreased drastically and mechanical stability increased reasonably. But the proton conductivity got decreased with the inorganic material. This is due to reduction in the number of conducting protons because of the formation of bond between sulphonic acid group and metal oxide. Compatibility of metal oxides with SPSEBS was obtained from AFM images. Even though it showed decrease in conductivity, all the composites showed good performance in PEM fuel cell than SPSEBS membrane and Nafion. This is due to presence of hydrophilic metal oxides in membrane.

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