

# EFFECT OF ADDITION OF TITANIUM DIOXIDE ON THE PROTON CONDUCTIVITY OF POLYSTYRENE MEMBRANE FOR FUEL CELL APPLICATIONS

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*Abstract-Proton conducting polymer electrolyte membrane is the most important component of polymer electrolyte membrane fuel cells (PEMFC). The positive effect of addition of oxo-clusters of Ti, Zr, W and hydrophilic additives like SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> on the proton conductivity characteristics of Nafion membranes have been reported earlier. Here we report the effect of additive titanium dioxide on the proton conductivity of polystyrene membrane in aqueous solution. The enhancement of proton conductivity was observed to be increase for titanium dioxide (by factors of 4.63). This showed that the proton conductivity was increased on addition of titanium dioxide in polystyrene membrane. The proton conductivities were calculated from the pH values measured at room temperature using an electrochemical cell and pH meter, on the basis of a proton transport model for porous membranes in aqueous solution. The membranes were characterized by FTIR, SEM and the observed results are explained in terms of the hydrophilicity of the additive.*

**Keywords**-Fuel Cell, Proton Conducting Membrane, Polystyrene, Titanium dioxide, Hydrophilicity

## I INTRODUCTION

Hetero-poly-acids (HPA) like phospho-tungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.nH<sub>2</sub>O), silicotungstic acid (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>.nH<sub>2</sub>O) and phospho-molybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>.nH<sub>2</sub>O) have been used as additives to Nafion and other polymer proton conducting membranes to improve proton conductivity[01-04]. These membranes showed a strong performance enhancement that increased with increasing temperature. However, upon heating HPA dehydrate and the conductivity drops sharply. HPA is highly water soluble and eventually leeches out from the polymer electrolyte membrane. Other drawbacks are their high cost and the adverse effects on the mechanical strength

of the membrane. The positive effects of addition of oxo-clusters of Ti, Zr, W on the proton conductivity characteristics have been reported earlier, where it was postulated that these oxo-clusters act as cross-linkers between the sulphonyl groups of Nafion membranes [5]. A lot of work has been done in Nafion membranes doped with hydrophilic inorganic additives like SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> [06-07]. It has been clearly established that these hydrophilic additives are very helpful in increasing the proton conductivities of Nafion membranes. We felt that the role of hydrophilic inorganic additives could also be studied along with solid acid additives. We chose TiO<sub>2</sub> instead of the others because of its many interesting characteristics. It is known to have a much higher hydrophilicity than SiO<sub>2</sub> because of its higher affinity to hydroxyl groups and it is also used as a photocatalytic agent in the oxidation of hydrocarbons in aqueous media [08-15].

## II EXPERIMENTAL

### (a) Preparation of Membranes

The membranes were prepared using the phase inversion method. Initially polystyrene granules were dissolved in DMF (dimethyl formamide) obtained from Qualigens Fine Chemicals (Product No. 23157) and then TiO<sub>2</sub> (Qualigens Fine Chemicals Product no 28375) in the weight ratio given in Table (01) were added to the polystyrene+DMF solution and continuously stirred using magnetic stirrers for one hour. To ensure better crosslinking in the membrane DVB (Divinyl Benzene, Sigma Aldrich, Catalog No 41,456-5) was added at 2.5 % by weight to the total weight of the polystyrene and additives. At the end of one hour of stirring at temperature 40° C, a uniformly viscous liquid solution containing polystyrene in dissolved form and the additives in suspended form was obtained. Then this casting solution was spread onto a glass surface with a controlled thickness using a doctor

blade. The glass with the wet film on top was then immersed in a nonsolvent bath (de-ionised water at room temperature). The solvent diffused into the precipitation bath, whereas the nonsolvent diffused into the cast film. After a time in which the solvent and the nonsolvent were exchanged, the polymer solution (wet film) became thermodynamically unstable and demixing took place. Finally, a solid polymer membrane formed with an asymmetric structure and peeled off from the glass. This membrane had two surfaces: the glass side surface and the water side surface. In general, pores close to the waterside surface were much smaller than those close to the glass side surface for an asymmetric membrane. The membranes prepared by the above phase inversion method were washed several times using deionised water to remove traces of DMF as also the loose additive particles sticking to the surface of the membrane. Then the membranes were dried in a desiccator at room temperature for 72 hours. The details of the weight compositions of the different constituents of the membranes prepared by us are given in Table 01.

| Membrane | Wt% of Constituents of the Membrane |                  |                  |
|----------|-------------------------------------|------------------|------------------|
|          | Polystyrene                         | Di-vinyl Benzene | TiO <sub>2</sub> |
| Ps       | 97.5                                | 2.5              | -                |
| Ps + TiO | 87.5                                | 2.5              | 10               |

**Table 1:** Weight Composition Of The Different Constituents Of The Membranes

### III RESULTS AND DISCUSSION

#### (a) Analysis of FTIR Spectra

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The IR absorption spectra for the membranes are shown in Figures (01-02). The spectra are useful in finding out the nature of chemical bonds among and within the different constituent molecules. They are also helpful in detecting the presence of hydrogen bonds in association

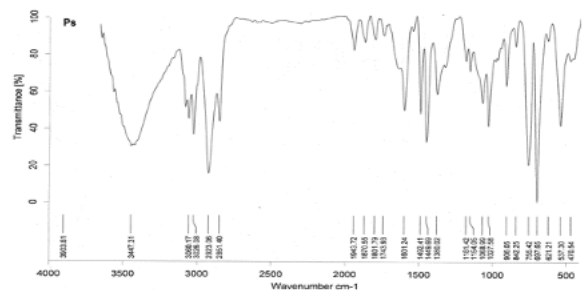
with water molecules and hydroxyl groups which are the major factors helpful in proton conductivity.

The following IR absorption bands indicate the presence of water and hydroxyl groups:

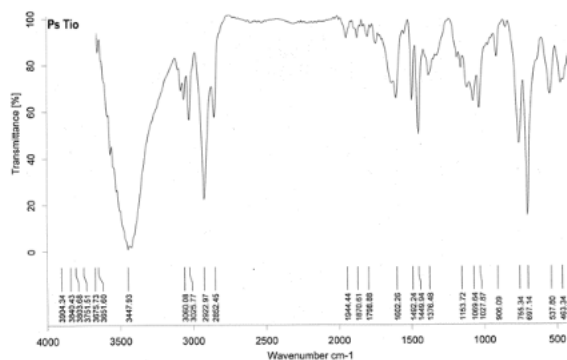
~3400-3600 cm<sup>-1</sup> strong wide and deep absorption bands arising from -OH stretching A sharp medium band at 1635 cm<sup>-1</sup> is attributed to aquo (H-O-H) bending. We analysed the FTIR spectra of the membranes on the basis of the above two absorption bands. The pure Ps membrane FTIR spectrum was used as the standard against which the comparisons were made of the FTIR spectra of other membranes. Our analysis is summarized in Table 02.

| Bands  | Ps  | Ps+TiO   |
|--|---|--|
| ~3400-3600 cm <sup>-1</sup> band relative to 2923 cm <sup>-1</sup> | 3447 cm <sup>-1</sup> broad but less deep; indicates presence of OH group | 3448 cm <sup>-1</sup> Broad but deeper; indicates more OH than (1)   |
| 1635 cm <sup>-1</sup> band   | Present and distinct; indicates H <sub>2</sub> O                          | Present, broader, distinct; indicates more H <sub>2</sub> O than (1)   |
| Other differences observed   |   | 652 cm <sup>-1</sup> (Ti-O-Ti); 1117 cm <sup>-1</sup> (O - di - substituted benzene); 3439 cm <sup>-1</sup> (TiO <sub>2</sub> -OH) |
| Remarks  | Pure Ps standard spectrum with some water                                 | Presence of hydrophilic TiO <sub>2</sub> has increased water content   |

**Table 2:** Summarized Analysis of FTIR Spectra Of Membranes



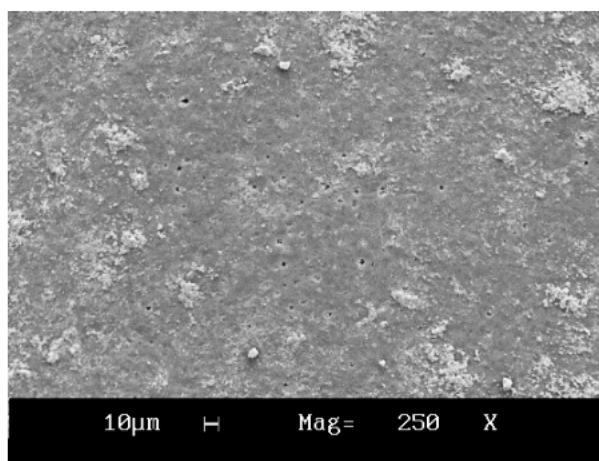
**Figure 01.** IR Spectrum Of Ps Membrane



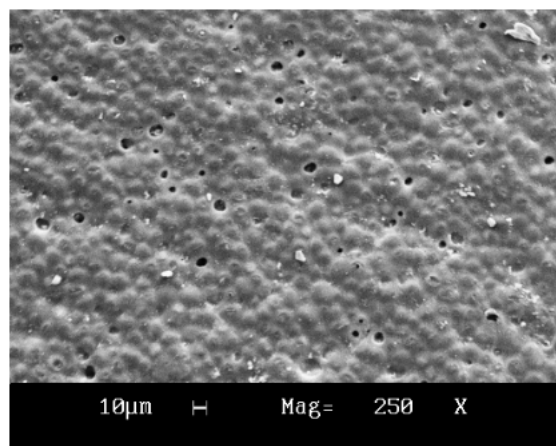
**Figure 2:** IR Spectrum Of Ps + TiO Membrane

**(b) Analysis of SEM Results**

The membranes display asymmetric character in terms of porosity. The water side of the membrane surfaces show dense character with the size of the pores much smaller compared to the other surface – the glass side of the membrane surfaces – which have a much more porous nature with larger size pores. The water sides are somewhat less smooth and undulating, whereas the glass side of the membranes are smoother and plainer. In the case membranes having additives, the additive particles sometimes are seen to lie inside the pores, obstructing/narrowing the pores. This depends largely on the diameter sizes of the additive particles. In our case we crushed the precipitates of the additives using mortar and pestle and then sieved them with a 150 μm sieve. The SEM images (Figures 03-04) show that the additive particle sizes are 50-60 μm maximum.



**Figure 4:** Water Side



(Glass Side)

**Figure 4:** SEM Surface Image Of Ps+TiO Membrane

**(c) Thickness, Water Uptake, Porosity**

From the experimentally determined thickness of the wet membranes and the weights of the dry and the wet membranes measured at room temperature ~30 oC, the water uptake and porosity of the membranes were calculated. The area of the membranes was taken as the area of the membranes exposed to the acid solution in the electro-chemical cell used for measuring proton transport. The results are summarized in Table 03.

| Membrane | Wet Thickness | Area              | volume of feed cell | Water Uptake | Porosity |
|----------|---------------|-------------------|---------------------|--------------|----------|
|          | 1 cm          | A cm <sup>2</sup> | V cc                | u %          | Por %    |
| Ps       | 0.025         | 3.02              | 15.9                | 242.86       | 71.83    |
| Ps + TiO | 0.020         | 3.14              | 15.9                | 220.34       | 71.79    |

**Table 3:** Water Uptake and Porosity of Membranes These results show that the water uptake and porosities of the membranes prepared by us were quite satisfactory. The SEM characterization also supports the highly porous nature of the membranes.

**(d) Proton Diffusivity and Conductivity**

To study the effect of additives on the proton conductivity of membranes, we started with pure Ps membranes with no functional groups like sulfonyl, phosphonyl etc.. in it. The advantage here is that, in pure Ps membrane proton transport will be basically bulk-like in character and hardly any surface conduction effect will be observed. Thus on adding an additive, there will be an extra contribution due to the surface conductivity of the additive. This will be easier to observe in a neutral membrane like Ps. Proton diffusivity  $D$  was calculated as  $D = P l$ , where  $P$  is the permeability coefficient and  $l$  is the membrane thickness.  $P$  was experimentally determined by using an electrochemical cell in which one cell contained feed solution (HCl conc.1M, Qualigens Fine Chemicals, Product No.-29145) and the other cell the stripping solution (distilled water at time  $t = 0$ ).

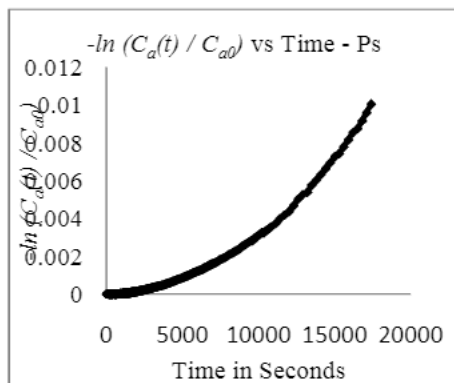
The following equation written in terms of the proton concentration in the feed cell, based on Fick's Law of Diffusion describes the permeability coefficient of proton ( $P$ ,  $\text{cm}^3 \text{cm}^{-2}\text{s}^{-1}$ ):

$$-\ln \left[ \frac{C_a(t)}{C_{a0}} \right] = (AP/V) t$$

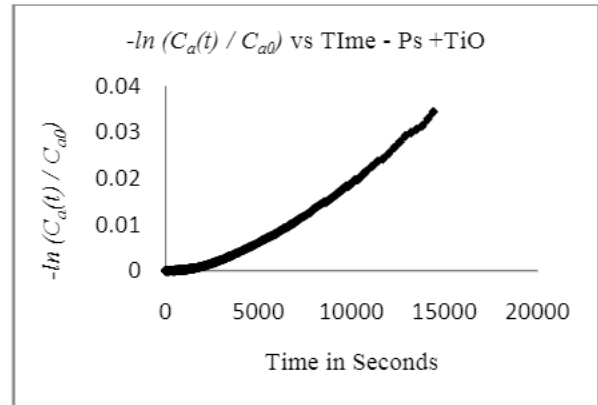
Where  $C_{a0}$  (mol/litre) is the initial concentration of the feed solution,  $C_a(t)$  (mol/litre) is the feed concentration calculated from the concentration of the stripping solution  $C_w(t)$  at time  $t$  (s) [16].

$$C_a(t) = C_{a0} - C_w(t)$$

$V$  is the feed volume (ml) and  $A$  is the actual membrane area ( $\text{cm}^2$ ). The plots of  $-\ln (C_a(t) / C_{a0})$  versus time  $t$ , from which  $P$  were calculated, are shown in Figures 05-06.



**Figure 5:** The Plot Of  $-\ln (C_a(t) / C_{a0})$  Versus Time For Calculating The Proton Diffusivity Of Ps Membrane.



**Figure 6:** The Plot Of  $-\ln (C_a(t) / C_{a0})$  Versus Time For Calculating The Proton Diffusivity Of Ps+TiO Membrane.

This value of  $D$  was then used to calculate proton conductivity according to Nernst-Einstein equation  $\sigma = (F^2/RT)D$ , where  $F$  is Faraday constant and  $R$  is the gas constant. Since the different membranes have differing porosities, we divided the conductivity values obtained from the Nernst-Einstein relation by the respective porosities. This way the effect of porosity was offset, so that the differences could now be attributed to solely the nature of the additives. The values of proton conductivity for the different membranes studied by us are given in Table 04.

| Membrane | Proton Diffusivity $D = \text{slope} \cdot V/A$ | Proton Conductivity $\sigma = (F^2/RT)D$ | $\sigma/\text{Por}$<br>S/cm | Relative<br>$(\sigma/\text{Por})$ |
|----------|---|--|-----------------------------|-----------------------------------|
|          | $\text{cm}^2/\text{sec}$                        | S/cm                                     |                             |                                   |
| Ps       | $4.24 \times 10^{-08}$                          | $1.57 \times 10^{-08}$                   | $2.18 \times 10^{-08}$      | 1.00                              |
| Ps + TiO | $1.96 \times 10^{-07}$                          | $7.26 \times 10^{-08}$                   | $1.01 \times 10^{-07}$      | 4.63                              |

**Table 4:** Proton Conductivity in Membranes

The table shows that the values obtained by us for the conductivities of the membranes are a few orders of magnitude lower than those reported in literature for sulfonated membranes such as Nafion. This is not surprising, since we have not used sulfonated/phosphonated membranes in our studies.

Whatever variations that are observed in the conductivities of the different membranes are thus

purely due to the additives present in the membranes. The following features may be noted:

The effect of adding TiO<sub>2</sub> to the membranes in all cases is to raise the conductivities of the membranes. In the case of pure Ps, its addition caused the conductivity to raise by nearly five times. FTIR spectra of TiO<sub>2</sub> membranes show higher hydrogen-OH and hydrogen-H-O-H bond absorption pointing to higher hydrophilicity of TiO<sub>2</sub>. Thus hydrophilicity of additives seems to play a very important role in proton conductivity. Similar effects were observed in the case of Nafion and other sulphonated membranes by others [05,16]. The same effect was noticed in Nafion for the case of a similar hydrophilic additive SiO<sub>2</sub> previously [17,18]. Our results show that substantial improvements in proton conductivity can be achieved by using TiO<sub>2</sub> as additive in the case of polystyrene membranes as well.

#### IV CONCLUSION

Our experimental results show that the addition of titanium dioxide has a very dramatic and positive effect on proton conductivity. Perhaps this is due to its much higher hydrophilicity as observed in the FTIR characterisations where ~3400-3600 cm<sup>-1</sup> band is seen to be strikingly enhanced for titanium dioxide added membranes.

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