PREPARATION AND CHARACTERIZATION OF CROSSLINKED PVA/TiO$_2$ HYBRID MEMBRANES CONTAINING SULPHONIC ACID GROUPS FOR DIRECT METHANOL FUEL CELL APPLICATIONS

Kanakasabai Panchanathan*, Prakash Nanjan Bellie**

*P.Kanakasabai, Salalah college of Technology, Salalah, Sultanate of Oman.
**N.B.Prakash, Salalah college of Technology, Salalah, Sultanate of Oman.

Corresponding Author: Prakash Nanjan Bellie, Salalah college of Technology, Salalah, Sultanate of Oman.

ABSTRACT
A polymer electrolyte membrane for direct methanol fuel cell was prepared by compositing PVA/sPTA membrane, with TiO$_2$ nanoparticles prepared by sol-gel process. The membranes were fabricated by varying concentration of SPTA (5% to 30% wt of PVA) and TiO$_2$ (2% to 10% wt of PVA) and crosslinking time (from 5 min to 60 min). Water uptake, proton conductivity, IEC (ion exchange capacity), and tensile strength of the membranes were determined to analyse the transport properties. Dynamic mechanical analysis (DMA) and thermo gravimetric analysis (TGA) were performed to determine mechanical and thermal stability of the membrane. Water uptake was calculated using weight gain method whereas the proton conductivity was characterized using a four-probe impedance spectrometer. Water uptake of the membranes changed with amount of sulphonation and either decreased or remained constant with the crosslinking time. It was observed that proton conductivity is dependent on sPTA concentration (as sPTA acts as both crosslinking agent and a proton donor). The proton conductivity of the PVA/sPTA/TiO$_2$ was measured to be in the range of 0.01-0.03 S/cm. The ion-exchange capacity (IEC) of the hybrid membranes was ciphered by general acid base titration. IEC values were observed to increase with the amount of sPTA added and remained independent of TiO$_2$ concentration. The chemical structure of the membrane was analysed by FTIR spectroscopy.

KEYWORDS sulphonated PVA membranes, sulphothalic acid, ion exchange capacity, proton conductivity, water sorption

INTRODUCTION
A direct methanol fuel cell (DMFC) is a proton exchange membrane constituted cell which uses methanol directly to generate electricity due to the redox reactions occurring at the anode and cathode. Methanol is supplied at the anode side which gets oxidised to produce protons, electrons and carbon dioxide. The electrons flow through the external circuit connected between the electrodes while the protons pass through the membrane to the cathode side. The protons react with oxygen, producing water as by-product. Water acts as a medium for proton conduction through the membrane. Methanol can also be transported across the membrane to the cathode by an electro-osmotic drag. This can be attributed to the dipole moment of methanol. This proves that proton conductivity and methanol permeability are two important factors determining the performance of the cell which in turn determine its efficiency. To improve the performance, it is necessary to increase the proton conductivity and reduce the methanol permeability through the membrane. Perfluorinated membranes such as Nafion$^{(R)}$ are currently used for DMFCs because of high proton...
conductivity (0.2 S/cm). But a major setback is its very high methanol permeability (10^{-6} \text{ cm}^2/\text{s}) and high cost which in turn reduces the cell efficiency drastically. Various membranes including sulphonated PEEK, sulphonated polysulphones, Nafion based composite membranes, composites containing Zirconium phosphates, zeolites and polyvinyl alcohol (PVA) based membranes have been developed and studied. It has been found that trying to improve one property of the membrane compromises on the other thereby having to make a balanced trade-off.

This research study deals with development of PVA composited membranes for DMFC. Polyvinyl alcohol (PVA) used for the membrane has been industrially prepared from Polyvinyl acetate (PVAc). PVA has inherent methanol resistance as it has been used in pervaporation processes that separate water-alcohol mixtures. However the main disadvantage with PVA is its hydrophilicity and lack of proton conductivity. Chanthad et. al [2] developed a membrane for DMFC by modifying PVA with Sulphopthalic acid where crosslinking time and concentration of sPTA were varied to produce the membranes. Water uptake tended to decrease with crosslinking time whereas proton conductivity, though lower than Nafion(R) and independent of crosslinking time was found to range from 0.024 – 0.035 S/cm. Methanol permeability values of the sulphonated PVA (10% sPTA) was found to be lower than that of Nafion(R).

In this study, properties of PVA/sPTA membranes modified with TiO$_2$ nanoparticles were studied. Albeit Titania is expensive, possibility of synthesising anatase TiO$_2$ in a mundane lab environment and its non toxic nature advocated the choice of Titania as filler material. PVA/sPTA/TiO$_2$ hybrid membrane was prepared by sol-gel process. sPTA acted as both crosslinking agent as well as proton donor. The crosslinker was added hoping to increase the proton conductivity of PVA and decrease methanol permeability. TiO$_2$ was added as filler, to improve the barrier to methanol crossover.

The synthesis of crosslinked poly (vinyl alcohol)/layered double hydroxide (PVA/LDH) hybrid membranes with solution casting method has been studied and the experimental results indicate that incorporating 20 wt.% LDH into the PVA resulted in not only a higher ionic conductivity, but also a lower ethanol permeability$^1$.

The study of nano sized titanium-dioxide (TiO$_2$) doped phosphonated polyvinyl alcohol (PVA) based membranes were synthesized and subjected to the characterization experiments such as, determination of water uptake capacity and ion exchange capacity, swelling properties, Fourier Transform Infrared Spectroscopy (FT-IR), fenton tests, mechanical tests and electrochemical impedance analysis (EIS). As a result of all these studies it was determined that the 15% TiO$_2$ doped membrane has the better properties such as highest proton conductivity (0.03 S.cm$^{-1}$ ), ion exchange capacity (1.04 meq.g$^{-1}$ ) and water uptake (45%)$^2$.

PVA (poly vinyl alcohol)-MnTiO$_2$ (PM) and PVA-PVP (poly 3 vinyl pyrrolidone)-MnTiO$_3$ (PPM) nanocomposite membranes have been prepared with solutions casting method. Glutaraldehyde (GA) was used as cross linking agent. The results showed that the proton conductivity and water uptake of the nanocomposite membranes due to hydrophilic nature of MnTiO$_3$ nanoparticles were higher than that of the PVA membrane$^3$.

Novel membrane of inorganic–polymer hybrid membrane was prepared by incorporation of the nano-TiO$_2$ into regenerated cellulose (RC). The resulting membrane was characterized by AFM, SEM, and XRD. TiO$_2$ particles formed on the surface and in the interior of the hybrid membrane due
to the TiO₂ conglomeration, and the surface roughness of the hybrid membrane increased linearly with increasing TiO₂ content.  

**MATERIALS AND METHODS**

Poly vinyl alcohol (PVA, 89% hydrolyzed, M₆= 85000 g/mol) was procured from SD Fine Chemicals Ltd., Mumbai, India. Sulfophthalic acid (Spta, 50% aqueous solution) and Titanium iso-propoxide was supplied by Sigma Aldrich, Mumbai, India. Methanol and nitric acid used was obtained from Finar Chemicals, Ahmedabad, India.  

**Preparation of nano-sized titanium dioxide**

Nanosized titanium dioxide was prepared by hydrothermal process. Titanium tetra iso-propoxide (12.5 ml) was mixed with 0.6 ml of 70% HNO₃ and 75 ml of distilled water in a flask. The solution was kept for vigorous magnetic stirring till flaky white precipitate is obtained. The white suspension is then heated to about 80°C-90°C for about 8 hrs while the stirring was maintained. This gives a colourless opaque solution. The flask is left uncovered during heating as the solution needs to be concentrated. The concentrated solution was then put in a Teflon digestion vessel and heated at 200°C for 10 hrs. TiO₂ sediments at the end of 10 hrs and water is filtered out from it. SEM (Scanning Electron Microscope) image of the TiO₂ prepared is shown in Fig 1.  

**Membrane preparation**

A 2% by weight to the polymer weight of TiO₂ is dissolved in water in a beaker and is magnetically stirred to 3-4 hrs to get a uniform solution thus ruling out the chances of agglomeration. TiO₂ concentration is varied from 2% to 10% by wt. 10% (wt) PVA is added to the mixture and stirred for 6 hrs at about 60°C. SPTA is added to the solution varying its concentration from 5% to 30% (wt basis of PVA) and stirred for 24 hrs at room temperature. This solution is then poured in an acrylic mould and kept in an oven for 12 hrs at 60°C for drying. Finally crosslinking is ensured by placing the dried membrane for given crosslinking time at 120°C. Thickness of the cast membrane ranged between 120 microns to 150 microns. The cast membrane is washed with de-ionized water prior to testing.  

**Membrane characterization**

Fourier transform infrared (FTIR) analysis of the membranes was performed to investigate the morphology of the membrane and to confirm the crosslinking of PVA/sPTA and presence of TiO₂ in the PVA/sPTA/TiO₂ membranes. For this IR wavelength operating in the range of 4000 cm⁻¹ to 500 cm⁻¹ was utilised.  

**Measurement of water uptake**

The sulphonated membrane was immersed in de-ionized water for 24 hrs. The excess superficial water on the membrane was removed a tissue paper and immediately weighed. The water content is calculated based on the difference between the wet weight and the dry weight with respect to the initial dry weight of membrane.

\[
\text{\% water uptake} = \frac{\text{weight}_{\text{wet}} - \text{weight}_{\text{dry}}}{\text{weight}_{\text{dry}}}
\]

where

- weight_{wet} is the wet weight of the membrane
- weight_{dry} is the dry weight of the membrane
Ion exchange capacity
Ion exchange capacity is calculated based on a titration technique. Firstly, the dry weight of the membrane is measured. The membrane is then immersed in 30 ml 0.1 N HCl for 16 hrs. Further, the membrane is cleaned with distilled water to remove excess superficial HCl. The sample is then immersed 30 ml 0.1N NaCl for 24 hrs. This solution is then titrated against NaOH with phenolphthalein as the indicator to evaluate the amount of H⁺ ions taken up by the membrane. The IEC value is calculated by the following equation:

\[
\% \text{IEC} = \frac{\text{number of milliequivalents of protons transferred}}{\text{dry weight of the membrane}}
\]

Proton conductivity
The conductivity of PVA/TiO₂ sulphonated membrane was measured using a four probe impedance spectrometer (Gill AC, Core Run i5) at a frequency of 1mHz. The membrane samples are immersed in de-ionized water for 12hrs prior to testing. The hydrated sample was then mounted onto the cell and an AC current of .01 mA was applied. The conductance of the sample was obtained from an AC potential difference between the 2 inner electrodes. The conductivity (σ) was calculated by using the following equation.

\[
\sigma = \frac{l}{RA}
\]

where σ is the proton conductivity (S/cm), l is the distance between the counter electrode and working electrode (cm), R is the bulk resistance of the membrane (Ω) and A is the cross-sectional area of membrane (cm²).

Dynamic Mechanical Analysis (DMA)
Mechanical stability of the membranes is determined using a dynamic mechanical analyzer, Seiko DMS 6100 at a frequency of 1 Hz at the rate of 2⁰C/min in an air atmosphere. The relaxation temperatures are determined from the corresponding peak temperatures on the damping (tan δ) curves.

Thermo Gravimetric Analysis (TGA)
TGA is performed for the membrane samples using Seiko TG/DTA 6200, EXSTAR 6000 under a 140 ml/min N₂ flow and a heating rate of 20⁰C/min. The loss in weight (%) is plotted against temperature and the empty pan is used as reference weight during the experiment.

Tensile Strength
Tensile testing of the membrane samples are performed using a Universal Testing Machine (UTM, by Zwick Roell) at a crosshead speed of 10mm/min, temperature of 25⁰C and 82% humidity. The gauge dimension is 10cm x 2cm and each membrane was measured in triplicate.

RESULTS AND DISCUSSIONS
PVA and sPTA has FTIR characterization peaks at 1029 cm⁻¹ and 1250 cm⁻¹ as shown in figure 2. A broad peak ranging between 2900 cm⁻¹ and 3600 cm⁻¹, representing hydroxyl group of PVA can be observed. A small sharp peak at 1725.45 cm⁻¹ corresponds to the vinyl acetate units of hydrolysed PVA molecules.
After the sulphonation new peaks have emerged at 1027 cm⁻¹ and 1239 cm⁻¹ corresponds to the Sulphur oxygen double bonds (both symmetric and asymmetric) of the modified PVA membrane. It
can be clearly seen that after sulphonation the peak around 1700 cm\(^{-1}\) is more intense. There is a broad peak around 3400 cm\(^{-1}\) that corresponds to the dilute sPTA solution used to prepare PVA-sPTA solution.

TiO\(_2\) has FTIR characterization peak at 500 cm\(^{-1}\). The PVA-sPTA-TiO\(_2\) FTIR peaks show a broad peak around 500-550 cm\(^{-1}\) and at 1300 cm\(^{-1}\) that corresponds to the sulphur oxygen double bonds. The above results confirm the presence of sulphonated group and the presence of filler TiO\(_2\).

Water uptake values of the membrane are shown in figure 3 and are a measurement of the hydophilicity of the membrane material. When a small volume of water is absorbed into a polymer, the water molecules primarily associate with the polar and ionic groups present in the polymer chain. At a certain volume of absorbed water, the polar and ionic groups become saturated. The maximum volume of bound water is typically dependent on the polarity and the content of ionic groups in the polymer. The water molecules occupy the space between the crosslinked structures and thus the swelling of the membranes take place. The water uptake characterizes the amount of water a membrane can hold in its saturated state.

In PVA-sPTA membrane the trend of the water uptake values highlight that the water uptake capability of the membranes tends to lower as the crosslinking time increases as evidenced from figure 4. Thus, during initial stages of crosslinking the water uptake values are found to be higher. But the decreasing trend shows that as the crosslinking time increases the crosslinking density increases. The crosslinking density is proportional to crosslinking time and hence the decreasing trend. Initially, there is an increasing trend of water uptake with the increase in % sPTA. Later, as the percent crosslinking increases the amount of crosslinking groups increases and thus resulting in higher crosslinking density. This explains why 30% sPTA has lower water activity than 10% sPTA.

Considering the PVA-sPTA-TiO\(_2\) membranes the nanoparticles added creates a significant change in the water activity of the PVA-sPTA membranes without filler. The trend is the decreasing with the concentration of sPTA and TiO\(_2\). Increase in the concentration of sPTA will have increased crosslinking density and thus a decreasing trend in water uptake. Addition of filler to normal PVA-sPTA membranes decreases the value further because the TiO\(_2\) particles are highly dispersible and thus will occupy the void sites of the crosslinking structure. This avoids the clustering of water molecules in the spaces and thus swelling of the membranes is reduced.

**Proton conductivity**

Proton conductivity is the most important transport property of the ion conducting polymer electrolyte membrane. It was observed from figure 5 that Proton conductivity of PVA-sPTA membranes does not change considerably with crosslinking time and concentration. The proton conductivity value ranges from 0.01-0.03 S/cm. Addition of TiO\(_2\) nanoparticles does not show any considerable variation in the value of proton conduction. The values are in the range of \(10^{-2}\) S/cm.

Figure 6 indicates that the crosslinking of PVA with sPTA is considered to have a low influence on the proton conductivity. According to vehicle mechanism, the free water can be act as a proton-carrying medium. However, the free water evaporates faster than bound water in a vaporized measuring condition. That is, the proton conductivity of PVA-sPTA did not improve much due to loss of the free water. The PVA/TiO\(_2\) hybrid membranes have relatively lower bound water than the PVA membranes. Thus, the proton conductivity is marginally lower in the case of filler containing membrane.
Ion Exchange Capacity

Ion exchange capacity of PVA-sPTA membranes increase with increase in the sulfophtalic acid content in the membrane, irrespective of the crosslinking time. This is obvious from figure 7 as the crosslinking increases the content of sulfophtalic acid increases and thus the ion exchange sites in the polymer.

In the case of PVA-sPTA membrane with the addition of filler the trend of increasing IEC values with respect to the sPTA concentration is seen, owing to the same reason that the sulfonic groups increases the ion exchange sites as observed in figure 8. But within the same % sPTA, ion exchange values decrease with increase in TiO$_2$ filler content. This can be attributed to the fact that the nanoparticles blocks the ion exchange sites, since exchange happens with hopping mechanism, in the crosslinked structure thus by reducing the ability of the proton transfer.

Figure 9 explains that there is no much effect of filler in PVA-sPTA membranes with regard to mechanical strength. But addition of sPTA to PVA lowers the values of the x-axis which confirms that the loss modulus value is decreasing with the crosslinker and the ratio of energy dissipated as heat to the energy lowered decreases with the addition of sulphonic acid groups. This value does not change much with addition of filler. It can be observed that DMA tests for PVA-sPTA membranes have proved high storage modulus values and that for PVA-sPTA-TiO$_2$, even higher storage modulus value is obtained. Due to crosslinked nature, the glass transition shifts to a higher temperature and the storage modulus is high for PVA-sPTA. At higher temperatures (greater than $130^0$C), it increases as a function of temperature indicating residual crosslinking reactions as indicated in figure 10.

Thermo Gravimetric Analysis (TGA)

Figure 11 shows that the first weight loss occurs around $160^0$C, and associated on the loss of absorbed water molecules. Most of the absorbed water molecules in the membranes are supposed to exist in a bound state, rather than in the free molecular state. The water molecules seem to have been bound directly to the polymer chains and/or the –SO$_3$H groups via hydrogen bonds. The PVA-sPTA-TiO$_2$ and PVA-sPTA membranes, the second weight loss region (occurring between temperatures $250^0$C –$400^0$C) corresponds to the loss of sulfonic acid from the sulfophahtalic acid, and the resulting breakage of the crosslinked bonds (i.e., the –CO–O– bonds). In the third weight loss region (at temperatures >$400^0$C), the polymer residues were further degraded at temperature above $500^0$C, which corresponds to the decomposition of the main chains of the PVA.

An increase in sPTA content induces more crosslinking in the PVA matrix, which leads to an increase in the residual char formed after temperatures of $700^0$ C. These results suggest that the degree of crosslinking and the introduction of silica into the PVA chains enhance the thermal stability of the given hybrid materials. The figure 12 shows that it is only 5% TiO$_2$ concentration. A low percent of nanomaterial could bring about a small change in the thermal properties at higher temperature. The thermal degradation decreases on the further addition of the TiO$_2$ filler.

Tensile Strength

The tensile strength and the modulus value of the membrane decreases numerously by the addition of sulfonic groups into normal PVA as indicated in figure 13. The tensile strength and elastic modulus is decreased further by increase of concentration of sulfophthalic acid. The addition of TiO$_2$ nanoparticles to the PVA-sPTA membranes had a tremendous effect on the mechanical strength of the membranes. The tensile strength and the elastic modulus of the PVA-sPTA-TiO$_2$ membranes is very high due to the inherent property of the nanoparticles of increasing the tensile strength. This is
attributed to the fact that the nanoparticles due to their small size and dispersive nature, tend to reinforce the membrane matrix thus increasing the mechanical strength of the membrane.

The tensile strength of PVA-sPTA 25% membrane is 3.4 N/mm² and the modulus value is 0.0272 N/mm². The addition of filler in the PVA based membranes shows a tensile strength of 12 N/mm², which are a 4 time increase and a modulus of 0.09 N/mm² which is evident from the above graph. Thus the addition of nanofillers reinforces the matrix of PVA-sPTA so effectively that the mechanical strength is significantly affected.

CONCLUSION

PVA was chemically modified with SPTA and titania was introduced as filler. To confirm the presence of crosslinking group the FTIR characterization was performed. It further conveyed that the addition of filler did not affect the crosslinking in the PVA/sPTA membrane. The water uptake and the ion exchange capacity have inverse trends in the case of PVA-sPTA membranes without filler. The water uptake values were decreasing due to the increase in crosslinking density but the crosslinking is a positive parameter for the ion transfer capability of the membrane. The IEC values increase with the crosslinking and sulfonic groups. The proton conductivity is in a range of 0.01-0.03 S/cm without showing a particular trend, as in no effect of crosslinking time or sulfonic group concentration. In PVA-sPTA membranes filled with TiO₂ nanoparticles, the water uptake value and the ion exchange values follow the same trend as the TiO₂ concentration decrease within a sulfonic group concentration but it had reverse trends as discussed for normal PVA membranes without filler as the sulfonic group increases. The addition of TiO₂ nanoparticles as a filler to sulfophthalic acid crosslinked polyvinyl alcohol membranes has no effect on the value of the proton conductivity. It shows no particular trend and lies in range of 10⁻² S/cm which was in agreement with the literature[2].

The thermal stability and the mechanical stability of the TiO₂ based sPTA crosslinked PVA membranes are high compared to that of the normal PVA-sPTA membranes without filler. The ultimate strength and the moduli values were found to increase due to the nanoparticles dispersion that mechanically reinforce the membrane matrix. The TGA results revealed that the thermal degradation of the membranes at higher temperature lowered with the addition of titania and DMA established the addition of titania fillers tend to increase the storage modulus of the membranes.

ACKNOWLEDGEMENTS

The authors sincerely thank The Dean, and the Head of Engineering Department, Salalah College of Technology, Salalah, Sultanate of Oman for their support in publishing this paper.

REFERENCES


Figure 1 SEM image of TiO₂
Figure 2. FTIR Spectroscopy
Figure 3. Water uptake of PVA/sPTA membranes
Figure 4. Water uptake of PVA/sPTA/titania samples
Figure 5. Proton conductivity of PVA/sPTA membranes
Figure 6. Proton conductivity of PVA/sPTA/TiO$_2$ membranes
Figure 7. IEC trend of PVA/sPTA membranes
Figure 8. IEC of PVA/sPTA/TiO$_2$ membranes
Figure 9. $\tan \delta$ vs. Temperature
Figure 10. Storage modulus vs. temperature
Figure 11. Loss modulus vs. Temperature

Figure 12. TGA of PVA/sPTA with and without TiO$_2$
Figure 13. Stress strain curve of PVA/sPTA and PVA/sPTA/Filler membranes

Table 1. Mechanical Properties of PVA-sPTA membranes

<table>
<thead>
<tr>
<th>% sPTA</th>
<th>Tensile Strength (N/mm²)</th>
<th>Youngs Modulus (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>7.45</td>
<td>0.075</td>
</tr>
<tr>
<td>20</td>
<td>3.45</td>
<td>0.0405</td>
</tr>
<tr>
<td>25</td>
<td>3.4</td>
<td>0.0272</td>
</tr>
<tr>
<td>30</td>
<td>2.425</td>
<td>0.0203</td>
</tr>
</tbody>
</table>