Preparation and characterization of a novel nano-size titanium oxide-PVA (TiO$_2$-PVA) composite ion exchange membrane

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Abstract. This paper presents the synthesis and characterization of Titanium oxide – polyvinyl alcohol (PVA) composite ion exchange membrane. The membrane consists of PVA as the base and titanium oxide, with different concentration, as the ionic conductor. The synthesised membranes were analysed on the basis of intermolecular interactions with the help of FT-IR spectroscopy. Characterization techniques such as SEM and TGA were carried out to analyse surface morphology and thermal properties of the synthesised membranes respectively. Transport number was obtained with the help of two compartment diffusion cell. Important parameters such as the water uptake and methanol uptake were also determined. The results were then compared to those available for a well-known commercial membrane called Nafion®. With the increase in the concentration of ionic conducting material from 0.1 g to 0.3 g in 100 ml of crosslinked-PVA solution, the transport number of the membrane increases from 0.86 to 0.89. Increase in the concentration of ionic conductor shows an insignificant effect on other properties like water uptake and methanol uptake and can be safely ignored. The transport number of the synthesized membranes were close to the transport number of Nafion, while the composite membrane performed better when it came to water uptake and methanol uptake as compared to Nafion.

Keywords— Composite Membranes, Cross-linked PVA, Ion Exchanger, Direct Methanol Fuel cell, Transport number, Methanol uptake, Water uptake.

1. Introduction
The most versatile and promising type of proton exchange fuel cells, which use methanol as a fuel, are the Direct Methanol Fuel cells (DMFCs). The main advantages of DMFCs are its compact size and the ease of transport of methanol which is energy dense liquid [3]. DMFC has high potential to replace lithium-ion batteries [2]. Proton exchange Membrane (PEM) is a type of membrane that only allows the transfer of protons and restricts the electrons transport. The efficiency of the DMFC depends, mainly on the quality of PEM. A good PEM must have very specific qualities such as good mechanical strength, thermal and chemical stability, high proton conductivity, high water uptake, low methanol uptake, and low methanol cross over [4]. Nafion is by far the best performing PEM in the market mostly due to its high proton conductivity. Although it is the most frequently used PEM, Nafion®, faces many drawbacks such as drop in performance at high temperatures (> 80 °C) and low humidity (< 30%), high methanol cross
over and relatively high cost [1],[7]. In order to overcome the drawbacks faced by Nafion®, researches are venturing other PEM materials to eliminate the drawbacks. One of the inexpensive material which has caught the attention of researches in recent past is Poly vinyl Alcohol (PVA). PVA is an organic polymer which has the capability to be used as a PEM. Some of the main characteristics of PVA which can be exploited are its hydrophilic nature, low methanol uptake, film forming capabilities, good mechanical stability and thermal stability [5]. Yinhui et al [5] and Jay Pandey et al [1] investigated PVA-based immobilised phosphotungstic acid membranes. The authors concluded that using PVA as base is very efficient and inexpensive way for synthesizing a proton exchange membrane. Some of the results shown by their synthesised membranes were very close to Nafion thus making PVA based membranes suitable for DMFC applications. Even though, PVA has most of the characteristics of a good PEM, it still lacks good proton conductivity. In order to enhance the proton conductivity of the PVA some other ion exchangers are blend with it to make a composite PEM. Usually, blending method is used to uniformly mix the crosslinked PVA matrix with ion exchange material to make a composite PEM. In this work, novel composite membrane was synthesised with simple blending method in which cross-linked PVA was blend with two different concentrations of titanium oxide as ion exchangers. Two composite PEM were synthesised, Fourier Transformation infrared spectroscopy (FT-IR) was performed to analyse the intermolecular interactions of the composite membrane. Other physico-thermal properties like surface morphology and thermal stability were analysed with the help of Scanning electron microscope (SEM) and Thermogravimetric analysis (TGA) analysis respectively. Transport number of the membranes were calculated and compared with Nafion. Other characteristic like water uptake and methanol uptake were also measured.

2. Experimental
2.1. Materials and chemicals for membrane preparation
Poly vinyl alcohol (PVA) (molecular weight: 14,000) and Glutaraldehyde (GA) (25vol %), were purchased from Rankem, India. Titanium oxide (99.5%, 80nm) (Nano shell, USA), other chemicals and consumables like hydrochloric acid (assay 35%), sodium hydroxide (NaOH) and acrylic sheet were purchased from Avantor, India.

2.2. Synthesis and characterisation of the membranes
2.2.1. Synthesis Membranes were synthesised in two steps. First, PVA aqueous solution was prepared by completely dissolving 5 % wt of PVA powder in 100 ml of deionized water with the help of magnetic stirrer for twelve hours at 60 °C. Crosslinkage was carried out by adding 1 ml of glutaraldehyde and 0.5 ml of HCl in the PVA aqueous solution for 30 min at 40 °C. Second step involved the blending of crosslinked PVA solution with two different concentrations of the titanium oxide. Two separate 100 ml beakers were filled with crosslinked PVA solution . In one beaker 0.1 g of titanium oxides and in other beaker 0.3 g of titanium oxide were added carefully while stirring with the help of magnetic stirred at 60 °C for an hour. Eventually, the solutions were casted on two different acrylic sheets and were placed in oven for eight hours at 60 °C to form the membranes.

2.2.2. Characterization FT-IR model (Carry -600) was used to analyze the final chemical structure of the composite membrane. TGA were obtained using (Mettler Toledo CH-8603) analyser. Samples around 10 mg were heated from 25 °C to 1000 °C at the rate of 10 °C min⁻¹. The experiments were carried out in nitrogen environment. SEM (Hitachi S-3600N) was used to study the surface morphology of the synthesised membranes.
The counter ion transport number was determined by measuring the potential difference between the two compartments of diffusion cell with 5 cm³ volume each. Counter ion transport number of the membrane can be calculated by Plank Henderson equation.

\[
t_+ = \frac{1}{2} \left[ 1 + \frac{nFE}{RT \ln \frac{C_1}{C_2}} \right]
\]

where \(t_+\) is the counter ion transport number, \(F\) is the Faraday’s constant 96,485 C mol\(^{-1}\), \(E\) is the membrane potential, \(R\) is the universal gas constant 8.314 J mol\(^{-1}\) K\(^{-1}\), \(T\) is the temperature in K, \(C_1\) is the higher concentration of NaCl solution (0.1M) and \(C_2\) is the lower concentration of NaCl solution (0.01M).

Methanol and water uptake were calculated with the help of following equation

\[
W_{\text{uptake}}(\%) = \left[ \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right] \times 100
\]

where \(W_{\text{uptake}}(\%)\) represents water uptake, \(W_{\text{wet}}\) represents the weight of membrane after hydrated with water, \(W_{\text{dry}}\) represents dry weight of membrane. Equation (2) is also used for calculating methanol uptake as well. To calculate the percentage uptake, first the membrane is dried completely in an oven at 50 °C for eight hours. After drying membrane is immersed in water for twelve hours then the membrane is removed from water and gently wiped with filter paper and weighed with the help of a weighing machine. At the end the same membrane is completely dried again in oven at 50 °C for eight hours and then weighed again to calculate the dry weight.

3. Results and Discussions

3.1. FT-IR Spectroscopy

The FT-IR spectra of 0.1 g TiO₂ membrane and 0.3 g TiO₂ are shown in Figure 1 and Figure 2 respectively. The crosslinking reaction and the presence of strong C-O-C stretching peaks at around 1110 cm\(^{-1}\) in the FT-IR spectrum confirms the formation of acetal linkage in the synthesised membranes. O-H stretching and –CH\(_3\) bending which are the characteristics of PVA were confirmed by the band around 3272 cm\(^{-1}\) and 2922 cm\(^{-1}\) [6]. Characteristic crystallization band for PVA remains same for all the membranes at around 1100 cm\(^{-1}\), thus confirming the presence of PVA in the membranes while as the presence of peaks at around 3297 cm\(^{-1}\), 1625 cm\(^{-1}\) and 670 cm\(^{-1}\) proves the presence titanium oxide.

![Figure 1. FT-IR analysis for 0.1 g TiO₂ membrane](image-url)
3.2. **TGA**

The TGA analysis for the synthesised membranes is shown in Figure 3. TGA curve shows the initial weight loss (10 %) up to 200 °C which attributes to loss of remnant water molecules present in the membranes. Two major degradation stages are seen in the membranes. The first one occurs around 285 °C - 325 °C which is associated to the rapid degradation of cross-linked PVA. And the second one is from 380 °C - 490 °C which is associated with the mild degradation of titanium oxide. As inorganic ion exchanger are stable at higher temperature, it is worth noting that there is a significant variation in the residual weight between the two membranes due to the difference in the concentration of the inorganic ion exchanger.

**Figure 2.** FT-IR analysis for 0.3 g TiO$_2$ membrane

**Figure 3.** TGA analysis of synthesised membranes in the temperature range of 25 °C to 1000 °C.
3.3. Water and methanol uptake

Table 1 shows the water uptake of the synthesised membranes at different temperatures. The percentage water uptake of the synthesised membranes were much higher compared to 29.2 % for Nafion 117 [7]. The water uptake of 0.1 g TiO$_2$ membrane at 30 °C is 36 % and at 40 °C it is 45 % while as the water uptake values for 0.3 g TiO$_2$ membrane at 30 °C is 35 % and at 40 °C is 42 %. The high water uptake is due to hydrophilic nature of PVA.

The methanol uptake of 0.1 g TiO$_2$ membrane is 9.2 % and 10.9 % at 30 °C and 40 °C respectively while as for 0.3 g TiO$_2$ membrane it is 9.5 % and 11.3 % at 30 °C and 40 °C respectively. Low methanol uptake is attributed to the methanol resisting properties of PVA. Both the synthesised membranes show better results than Nafion -117 which has the methanol uptake of 16.5 % [7].

Table 1. Water and methanol uptake of the synthesised membranes

| Name                  | Water uptake % | Methanol uptake % |
|-----------------------|----------------|-------------------|
|                       | 30 °C | 40 °C | 30 °C | 40 °C|
| 0.1 g TiO$_2$ membrane| 36    | 45    | 9.2   | 10.9 |
| 0.3 g TiO$_2$ membrane| 35    | 42    | 9.5   | 11.3 |

3.4. SEM

The microstructure of 0.1 g TiO$_2$ membrane is shown in Figure 4 (a) and for 0.3 g TiO$_2$ membrane in Figure 4 (b). The distribution of titanium oxide is fairly uniform in the PVA matrix. The nano structure is mainly compact, fracture free and without any sub-micron sized holes. It can also be noticed, with the increase in the concentration of titanium oxide there is an obvious aggregation mainly due to the bulk formation of titanium oxide during synthesis and can be seen as white dots in Figure 4 (b).

![Figure 4](image_url)

**Figure 4.** SEM image of (a) 0.1 g TiO$_2$ membrane (x4000) and (b) 0.3 g TiO$_2$ membrane (x4000)

3.5. Transport number

Various experiments were performed on two compartment diffusion cell to measure the membrane potentials. Eventually the average of the potential where calculated. That average was used to calculate the membrane counter ion transport number with the help of Plank's Henderson equation. Table 2 shows the calculated transport number and measured average membrane...
potential. The transport number of the synthesised membranes are very close to the transport number of Nafion-117 (0.96)[1].

Table 2. Transport number of synthesised membranes.

| Name               | Average membrane potential (mV) | Transport No | Temperature (°C) |
|--------------------|---------------------------------|--------------|-----------------|
| 0.1 g TiO₂ membrane | 42                              | 0.86         | 24              |
| 0.3 g TiO₂ membrane | 46                              | 0.89         | 24              |

4. Conclusion
A series of (TiO₂-PVA) composite ion exchange membranes were successfully synthesised for direct methanol fuel cells applications. The study reveals the possibilities of the synthesis of low cost ion exchange membranes. In summary, the synthesised membranes were characterised through FT-IR, SEM, and TGA. FT-IR spectra indicates the complex molecular interactions; SEM micrograph of the membranes shows defect free surface of the membrane without any fractures and holes. The thermal stability of the membranes was analysed with the help of TGA. Synthesised membranes possesses fair electrochemical properties with maximum transport number of 0.89. Water uptake to methanol uptake ratio was higher as compared to Nafion 117, due to hydrophilic and methanol repelling properties of PVA. The membranes prepared from Titanium oxide – poly (vinyl alcohol) are tailor-made for DMFC purposes because of their fairly high transport number, good thermal stability and relatively decent water to methanol uptake ratio.

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