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Preparation and Characterization of Nano-size Gamma Alumina (γAl_2O_3) and PVA Composite Membranes

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Abstract—*Two composite ion exchange membranes 80 µm in thickness were synthesized by solution casting method. In both the membranes crosslinked PVA is used as base/ support while as gamma alumina is used as inorganic ion exchanger. FTIR characterization was performed to determine the functional groups present in the synthesized membranes, SEM was used to study the morphology of the synthesized membranes, and the transport number of the membranes was obtained using two compartment diffusion cells. Water uptake and methanol uptake were also measured.*

Keywords*: Composite membranes, Cross-linked PVA, Ion Exchanger, Direct Methanol Fuel cell.*

1. INTRODUCTION

For past few decades there has been a through advancement in the field of membranes. Membranes are semipermeable materials which allow certain desired chemical/electrical entity to pass while insulating undesired ones. These membranes are used for variety of application, for example, electrolysis, electro-dialysis and fuel cells [7].

Direct Methanol Fuel cells (DMFC) are one of the applications in which ion exchange membranes are used to generate electric current. DMFC is a type of fuel cell in which chemical energy is converted to electrical energy with the help of certain chemical reactions wherein methanol is used as fuel. In DMFC cation exchange membranes are used as an electrolyte for proton transfer [3, 4, 6].

Cation exchange membrane is a category of membranes which only allow the transport of cations while as they have high insulation towards anions. Permeability of cations through the cation exchange membrane governs the performance of the membrane. Higher the cation transport though the cation exchange membrane, the better the performance of the cation exchange membrane, eventually increasing the performance of DMFC. Cation exchange membranes are commonly known as proton exchange membranes (PEM).

The performance of a good PEM does not only depend on proton transport, but it also depends on many other factors including low methanol crossover, chemical/thermal stability and mechanical strength [8]. Nafion is the most commercialized PEM available due to its high proton conductivity, good chemical thermal stability and high mechanical strength [1, 3].

Despite the good properties of Nafion, it does faces many drawbacks including severe drop in proton conductivity at high temperatures (<80^{o}C) and low humidity (>30 %) and cost. All these drawbacks forced researchers to explore other types of membrane materials, to overcome the drawbacks of Nafion in one or the other form.

Several composite membranes are reported by blending organic and inorganic materials to obtain the desirable results. PVA, an organic polymer, is the focus of attention as a strong base/support for the composite membranes due to its film forming features, high water absorption, low methanol absorption, good mechanical strength, good chemical /thermal stability and low cost.

Even though PVA has most of the desirable characteristics that a good PEM must have, it lacks in the basic property of proton conductivity [5]. Therefore, PVA cannot be solely used as PEM unless it has been treated with some other materials which have high proton transport properties. Blending is one the most commonly used techniques to synthesize composite PEM. Blending is a simple technique of mixing crosslinked PVA aqueous solution and ion exchangers with the help of magnetic stirrer [1].

2. EXPERIMENTAL

2.1 Materials and chemicals for membrane preparation

Poly (vinyl alcohol) (PVA), Glutaraldehyde (GA), Aluminium nitrate (Al $(NO_3)_3.9H_2O$, 98%) were supplied by Rankem, India. Ammonium bicarbonate (NH_4HCO_3, 98%) was purchased from SRL Pvt. Ltd. Other material and chemicals

like HCl (assay 35%), NaCl and acrylic sheet were supplied by local vendor.

2.2 Preparation of Nano-size Gamma Alumina γAl_2O_3 and PVA - γAl_2O_3 composite membranes

The materials and methods for the preparation of nano sized gamma Alumina were adapted from [2]. Crosslinked PVA was prepared by dissolving 5% wt PVA in 100 ml of deionised water for 12 hours at 60 ^oC. Crosslinking was done by using 1ml of glutaraldehyde and 0.5 ml of HCl. Two beakers of 50 ml each were filled with crosslinked PVA solution. In one beaker 0.3 mg nanosized gamma alumina was added and in other beaker 0.5 mg nanosized gamma alumina was added and then stirred for 4 hours at 60 ^oC. Eventually the solutions were casting on two different acrylic sheet to form a thin film and heated in an oven at 50 ^oC for 3 hours. Once the solutions dried to form films, which were then pealed from the acrylic sheets and were named as shown in Table 1.

Table 1: Name of the synthesized membranes

S.no	Polymer Used	Ion exchanger by weight.	Name
1	50 ml Cross-linked PVA	0.3 gm γAl2O3	0.3 mg Gamma alumina-PVA
2	50 ml Cross-linked PVA	0.5 gm γAl2O3	0.5 mg Gamma alumina-PVA

3. CHARACTERIZATION

3.1 Structural characterization

The structural characterization of the synthesized membranes were performed with FT-IR (Carry-600). Scanning electron microscope (SEM) (Hitachi S-3600N) was used to observe the micro structure of the synthesized membranes. Transport number was calculated with the help of two compartment diffusion cell.

3.2 Water uptake and Methanol Uptake

Water uptake and methanol uptake was calculated with the help of Equation 1.

$$\textbf{Water uptake}\ (\%) = \frac{(\textbf{W wet} - \textbf{W dry})}{\textbf{W dry}} \times\ \textbf{100} \qquad (1)$$

First the membrane is dried properly in an oven at 40 ^oC for three hours then immersed in deionized water for 12 hours. Then the membrane is removed from de-ionized water, slightly wiped with filter paper to remove extra water and then weighed (W wet). After that the soaked membrane is dried again at 50 ^oC for three hours and then weighed again to get dry weight (W dry). Water uptake was calculated by putting the measured values of Wwet and Wdry in equation 1. Same procedure was used to calculate methanol Uptake wherein deionized water was replaced by methanol.

3.3 Transport number

Two compartment diffusion cell was used to measure the potential of the membrane. Each compartment was of 5 cm^3 in volume. One compartment was filled with 0.1M NaCl solution and the other compartment was filled with 0.01M NaCl solution. The membrane was inserted in-between the two compartments with an exposed area of 3.14 cm^2. Ag/AgCl electrodes of 0.21mm were used. The transport number of the membrane with the help of Plank Henderson equation (Equation 2) was calculated.

$$t_+ = \frac{1}{2}\{1 + \frac{nFEn}{RTln\frac{C_1}{C_2}}\} \qquad (2)$$

where t_+ is the counter ion transport number, F is the Faraday's constant 96,485 $Cmol^{-1}$, E_n is the membrane potential, R is the universal gas constant 8.314 $Jmol^{-1}K^{-1}$, T is the temperature in Kelvin, C_1 is the higher concentration of NaCl solution (0.1M) and C_1 is the lower concentration of NaCl solution (0.01M).

4. RESULTS AND DISCUSSION

4.1 FT-IR Spectroscopy

Fig. 1 (a) and Fig. 1 (b). represents the FT-IR spectra of 0.3 mg Gamma alumina-PVA and 0.5 mg Gamma alumina-PVA respectively. The formation of acetal linkage was confirmed from both the crosslinking reaction and by the strong C-O-C stretching peaks at 1110 cm^{-1} in the FT-IR spectrum. The band around 3275 and 2940 cm^{-1} represents O-H stretching and $-CH_3$ bending which are the characteristics of PVA as shown in Fig. 1 . Peaks at 1103 cm^{-1} and 1400 cm^{-1} corresponds to gamma alumina in 0.3 mg Gamma alumina-PVA and 0.5 mg Gamma alumina-PVA (Fig 1.)

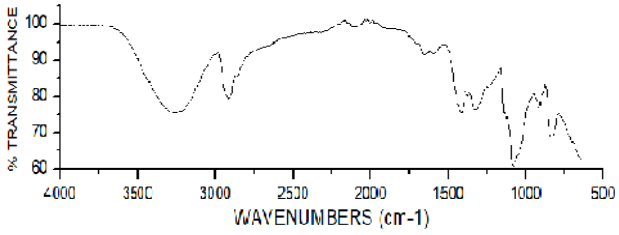

Figure 1 (a). FT-IR spectra of 0.3 mg Gamma alumina-PVA membrane

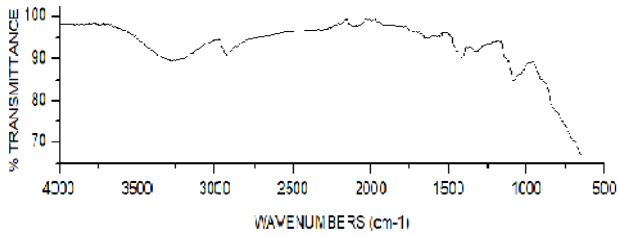

Figure 1 (b). FT-IR spectra of 0.5 mg Gamma alumina-PVA membrane.

4.2 SEM-EDS

SEM was used to investigate the surface morphology of the synthesized membranes. In Fig. 2 (a) and Fig. 2 (b) we can see that the inorganic particles are distributed uniformly in the polymer matrix. There are no holes in the membranes thus confirming the dense structure. Some aggregation can be also seen but they are mainly due to bulking of inorganic ion exchangers. EDS (Table 2) was performed to identify the element composition of the synthesized membranes. Mostly the membrane consists of carbon and oxygen due to PVA. Small traces of aluminium were also found which are present due to alumina.

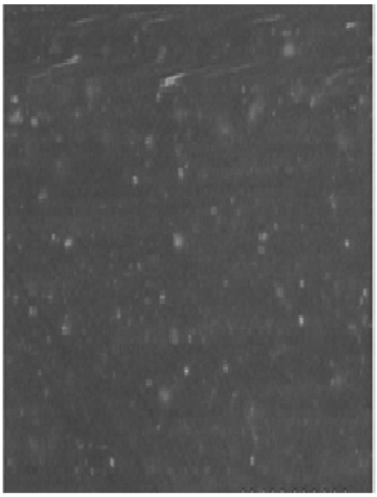

Figure 2 (a) . SEM images of the top view of the synthesized membranes: 0.3 mg Gamma alumina-PVA membrane (×1200)

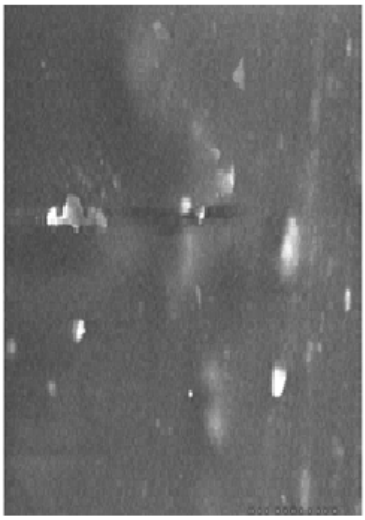

Figure 2 (b) . SEM images of the top view of the synthesized membranes: 0.5 mg Gamma alumina-PVA membrane (×3000)

Table 2: Atomic percentage of element present in the composite membrane

Name	Carbon (%)	Oxygen (%)	Aluminium (%)	Total (%)
0.3 mg Gamma alumina-PVA	47.07	52.23	0.7	100
0.5 mg Gamma alumina-PVA	27.29	71.91	0.8	100

4.3 Water and methanol uptake

Water uptake and methanol uptake plays a vital role in the performance of the PEM. PEM must be properly saturated with water to increase the proton conductivity. On the other hand, there should be less Methanol uptake. The data on methanol uptake and water uptake is given in Table 3.

Table 3: Water uptake, methanol Uptake of the synthesised membrane.

Name	Water Uptake (%)	Methanol Uptake (%)
0.3 mg Gamma alumina-PVA	204	40
0.5 mg Gamma alumina-PVA	288	38

4.4 Transport Number

Various experiments were performed on two compartment diffusion cells to obtain the potential difference between the two compartments of diffusion cell at different temperatures. Eventually the mean of those potentials was used to calculate the transport number of the membrane with the help of Plank Henderson equation as recorded in the Table 4.

Table 4: Counter ion Transport number of synthesised membranes.

Name	Average membrane potential (V)	Counter ion Transport number	Temperature
0.3 mg Gamma alumina-PVA	0.036	0.802	24oC
0.3 mg Gamma alumina-PVA	0.039	0.820	26oC

5. CONCLUSION

The study reveals the possibility of synthesis of PEM membranes by physically blending inexpensive organic and inorganic materials. With the increase in the content of inorganic ion exchanger in the PVA matrix, it is worth pointing that the water uptake and transport number of the membrane increased. FT-IR results clearly shows the interaction between the Crosslinked PVA matrix and inorganic ion exchangers. SEM results indicated the smooth structure of

the membrane and uniform distribution of ion exchanger in the polymer matrix. The synthesized membranes have comparable results with Nafion. The transport number of the synthesized membranes are very close to Nafion (0.92), it is evident from the results that the water uptake is much better in the PVA based membranes than Nafion because of PVA's hydrophilic nature while as methanol uptake is slightly better than Nafion. Although the synthesized membranes does not offer significant improvement over Nafion as far as transport no is concern but they do have some improvement when it comes to water uptake and methanol uptake.

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