Studies on PVA based nanocomposite Proton Exchange Membrane for Direct methanol fuel cell (DMFC) applications

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Abstract. Different concentrations of Poly (vinyl alcohol)/Montmorillonite (PVA/MMT) based proton exchange membranes (PEMs) have been prepared by solution casting method. The structural and electrical properties of these composite membranes have been characterized by using X-ray diffraction (XRD), Fourier transform infrared spectroscopic (FTIR) and AC impedance spectroscopic methods. The conductivity of the PEMs has been estimated for the different concentration of MMT. Water/Methanol uptake measurement were also analyzed for the prepared PEMs and presented. The proton conductivity studies were carried out at room temperature with 100% of humidity.

1. Introduction

Two challenges for humanity in the next 20 years are the striking availability of fossil fuels and global warming that result from the ever increasing use of fossil fuels. One possible solution to these problems is to use hydrogen as energy carrier. Fuel cell is an alternative for traditional energy sources because it provides ultra clean environment. The preparation of proton exchange membrane for fuel cells has been active research for the past one decade. Direct methanol fuel cells (DMFC) have received lot of attention because of their high energy density and low emission of pollutants. Methanol crossover in DMFC causes a loss of fuel and in turn it reduces the performance of DMFC. These drawbacks gave way to find new materials to minimize the methanol crossover through PEMs while maintaining good proton conductivity. Nafion, a commercially available membrane has a high chemical and electrical resistance as well as high proton conductivity. However it has been found that 40% of methanol can be lost across the Nafion membrane in DMFCs [1, 2]. So Nafion is not an effective barrier to methanol crossover. Therefore, a PEM with significantly decreased methanol crossover need to be developed. Composite membranes have been prepared by introducing nano-sized
inorganic materials, such as clay nanoparticles [3-8]. New cross-linked Nafion-PVA composite polymer electrolyte membrane has been prepared [Shao et al.]. It was found that the methanol permeability was reduced by about 48% [3]. Son et al. reported that poly (vinyl alcohol) based polymer electrolyte membranes containing polyrotaxane and the size of the polyrotaxanes play an important role in proton transport and methanol crossover in DMFC [4]. Yang has fabricated poly (vinyl alcohol)/montmorillonite/ poly (styrene sulfonic acid) proton conducting membranes for DMFCs [5]. It is noticed that, there is an enhancement of ionic conductivity due to the presence of –SO3H group in modified MMT fillers and PSSA polymer. Moreover this composite membrane exhibited a good electrochemical performance and it will be a potential candidate for DMFC in near future. In this work, PVA based nanocomposite proton exchange membranes were prepared by solution casting method and it is characterized for DMFC.

2. Experimental

2.1. Materials
Poly (vinyl alcohol) (Average MW~1,15,000) was purchased from Loba, India and it used as a host material. Montmorillonite K10 (Na+MMT) obtained from Hamada, India were used as recieved. Ion exchange resin obtained from Central Drug House (P) Ltd, India.

2.2. Preparation of protonated Montmorillonite (H’ MMT)
Montmorillonite (Na’ MMT) was dispersed in distilled water at room temperature. The dispersed solution was passed through the ion exchange resin which was taken in a burette for at least four times to ensure a complete exchange into H’. Then the collected protonated solution was dried at room temperature for several hours. The dried protonated MMT was grinded well using a mortar. Now the nano size protonated powder is ready for membrane preparation.

2.3. Preparation of Polymer Electrolyte Membrane
The composite membranes were prepared with appropriate weight ratios of PVA and MMT fillers. The host polymer and MMT clay were mixed in distilled water by normal stirring for 12 hrs in order to obtain homogeneous solution. The resulting solution was poured onto a glass plate or Petri dish. It was allowed to evaporate at room temperature. After complete evaporation of the solvent, the composite polymer membranes were peeled off from the Petri dish or glass plate. The thickness of the prepared composite polymer membrane is around 0.08- 0.12 mm. The prepared membranes were subjected to characterization.

2.4. Preparation of Sulfonated PVA/ MMT Membranes
The sulfonated composite solid polymer membranes were prepared with different molar concentrations of sulfuric acid. The prepared composite membranes were immersed separately in 5M, 8M and 10M solutions for at least 24 hrs at room temperature.

3. Results and discussion

3.1. FTIR analysis
The FTIR technique is used to find out the presence of chemical groups in the composite polymer electrolyte membranes and they were recorded in the range of wave number from 4000 to 500 cm⁻¹. Figure.1 shows, the FTIR spectra from PVA/ MMT composite polymer electrolyte membranes. It shows strong characteristic peaks of the PVA polymer at 1440, 1711, 1145, 920 and 853 cm⁻¹[6, 9, 10]. It can be seen that, the broad transmission peak of the O-H stretching bands at around 3600-3200 cm⁻¹ due to the strong hydrogen bonding of (water) intramolecular or intermolecular type. The vibration peak of C-H band at 2945 cm⁻¹ refers to the stretching of alkyl groups and the transmission peak at
1711.63 cm\(^{-1}\) arises due to the asymmetric stretching vibration of carbonyl (C=O) from the acetate group. Additionally, the strong peak at 1140.33 cm\(^{-1}\) is due to the C-O stretch, C-C stretching vibration. In addition, there were several vibrational peaks at 919.50 and 853.21 cm\(^{-1}\) were due to the C-C stretching.

3.2. XRD analysis

The X-ray diffraction patterns were taken by X-ray diffractometer. Radical scan were recorded in the reflection scanning mode with 2\(\theta\) being changed from 10\(^0\) to 60\(^0\). Figure 2 Illustrates the diffraction pattern of PVA/MMT composite polymer membranes that were prepared by adding with varied amounts of Na\(^{+}\)MMT and H\(^{+}\)MMT fillers. The pure PVA polymer is well known to exhibit a semi-crystalline structure with a large crystalline peak at a 2\(\theta\) angle of 19-20\(^0\). The peak at 19.6\(^0\) is correspond to the (101) plane in the pure PVA film [8]. It is observed that the same peak for PVA/20wt.% MMT composite membrane shows there is no crystalline peak in Figure. 2(e) because, the intensities of the (101) peak for PVA/MMT composite membranes were greatly reduced when the amount of modified MMT fillers increased. Under such circumstances, it was clearly observed that the amorphous phases existed in the PVA/MMT composite membrane. Therefore, the PVA/MMT composite membranes show good ionic conductivity for the higher concentration of nanoparticles. This is due to the more amorphous phases and more flexible of local PVA chain segmental motion in the PVA/MMT composite membranes.

3.3. Water /Methanol uptake analysis

The composite polymer membranes were kept at room temperature and weighed accurately with high accuracy electronic weighing balance. The selected membranes were taken for water and methanol uptake measurement. The uptake measurements of samples were calculated for different timing like 30, 60,120,180,240,300 and 600 seconds. The percentage of water uptake have been calculated by an equation

\[ WA\% = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100 \quad (1) \]

where, \(W_{\text{wet}}\) is the weight of the wet membrane; \(W_{\text{dry}}\) is the weight of the dry membrane.
Figure 3. Variation of water uptake of PEMs as a function of time.

Figure 3 shows that, the percentage of water uptake with respect to time. The concentration of MMT increases the hydrophilicity of the polymer membranes decreases in weight percentage. Because, protonated MMT to enhance acidity and hydrophilicity. Further, the hydrophilic nature of the membranes depends on the number of available protonated particle in acid groups and their dissociation capability in water. It is observed that the low concentration of MMT leads to absorb more water molecule so that the weight percentage of membrane shows good affinity with water.

Figure 4. Variation of 2M% methanol uptake of PEMs as a function of time.

Figure 5. Variation of 5M% methanol uptake of PEMs as a function of time.

Similarly, the percentages of methanol uptake of PVA/MMT composite membranes are shown in Figure (4-5) for different molar concentrations like 2M and 5M. From these, by increasing amount of MMT concentration, the methanol uptakes of the composite polymer membranes were decreased. In different concentration of methanol solution, PVA (90)-MMT (10) with protonated membrane shows lower methanol uptake. After 300 seconds the methanol uptake gets saturated for all the prepared samples. Thus, the results show that, the protonated membranes are suitable for DMFC applications.

3.4. Proton Conductivity analysis

The conductivity measurements were made for the PVA/MMT composite polymer electrolyte membranes by an AC impedance Analyzer. The composite polymer membranes were immersed in 5M, 8M, and 10M of H₂SO₄ solutions for at least 24 hrs at room temperature before measuring the conductivity measurement. The PVA/MMT composite polymer electrolyte membranes were placed between stainless steel, with surface area about 2.99 cm². The proton conductivity of composite
polymer electrolyte membranes was recorded at room temperature. The proton conductivity ($\sigma$) is given by

$$\sigma = \frac{l}{R_{dw}}$$  \hspace{1cm} (2)$$

where, $l$ is the distance between the two stainless steel electrodes; $d$ and $w$ are the thickness and width of composite PEMs; $R$ is the measured resistance of the membranes.

**Figure 6.** Variation of proton conductivity as a function of MMT concentration.

In Figure 6 the MMT concentration vs. conductivity of PVA/Na⁺MMT polymer membranes without sulfonation and with sulfonation (5M, 8M, 10M). It is observed that the MMT concentration increases with PVA, the conductivity values initially increased up to 10% of MMT, further it is decreased in conductivity at room temperature (Table 1). The proton conduction occurs by the hoping of protons because of an acid-base complex is formed between the acidic sulfonic groups of the polymer electrolyte and basic group of the MMT compound. On the other hand, this mechanism is disfavored by the increase of MMT content in the membrane because more basic than acidic groups are present at the composite membranes without ion exchange. As a result PEMs became anionic.

**Table 1. Proton conductivities of PEMs at varied amount of Na⁺MMT and H⁺MMT**

| Concentration of MMT | Conductivity S/Cm | Conductivity S/Cm | Conductivity S/Cm | Conductivity S/Cm |
|----------------------|-------------------|-------------------|-------------------|-------------------|
|                      | without Ion Exchange resin | with Ion Exchange resin | without Ion Exchange resin | with Ion Exchange resin |
|                      | PVA | 5% Sul-PVA | 8% Sul-PVA | 10% Sul-PVA | PVA | 5% Sul-PVA | 8% Sul-PVA | 10% Sul-PVA |
| 5                    | 0.0019 | 0.0096 | 0.2510 | 0.7587 | 0.0017 | 0.1297 | 0.2439 | 0.5326 |
| 10                   | 0.0022 | 0.1053 | 0.4730 | 0.9620 | 0.0021 | 0.1106 | 0.4114 | 0.8207 |
| 15                   | 0.0017 | 0.1816 | 0.4071 | 0.8240 | 0.0016 | 0.1437 | 0.5322 | 0.9417 |
| 20                   | 0.0027 | 0.1735 | 0.3203 | 0.6053 | 0.0006 | 0.1376 | 0.5371 | 0.9572 |

The conductivity of PVA/H⁺MMT composite membranes with different molar concentration of sulfonation is another beneficial effect. It is noticed that the increasing amount of MMT fillers as well as the conductivity also increases. This may be due to protonated MMT particle with sulfonic acid groups. The increase in Proton conductivity wrap up by addition of H⁺MMT fillers, is most likely due to the beneficial effect of the acidic -SO₃H terminal groups. From these above observations it is noticed that the proton conductivity value of 0.9572 S cm⁻¹.
4. Conclusion

The Protonated and non-protonated MMT with PVA Membranes were carried out. The proton conductivity value around 10-1S/Cm of PVA (80)-MMT (20) obtained at room temperature with 100% humidity. In the structural studies, we obtained amorphous phase in the higher concentration of H+MMT. It shows that, the MMT fillers are dispersed well in the polymer matrix. The above conductivity result is higher than that of Yang et al. reported for the same material.

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