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# SULFONATED GO/PVA NANO FIBROUSCOMPOSITE MEMBRANE AS PROTON EXCHANGE MEMBRANE

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## Abstract

In the present study the nanocomposite membrane were fabricated from Graphene oxide/ Polyvinyl alcohol (GO/PVA),Sulfonated Graphene oxide /Polyvinyl alcohol (SGO/PVA) nanofibers via electrospinning. Nanofibers were aimed to fabricated to develop the Chemical, thermal and mechanical stability of the composite membranes.The fabricated membranes were characterized using Scanning Electron Microscope (SEM), XRD and Thickness. Due to the strong interactions between the polymer and the metal oxide nanoparticle will embedded in the SGO/PVA composite. As a result, investigated SGO/PVA nanocomposite membranes have good potential for the Proton Exchange Membrane and it enhance the Proton Exchange Membrane Fuel Cells.

**Key word**: Electro spinning, Graphene oxide, Nanofiber, Sulfonated Graphene oxide

## 1. INTRODUCTION

In a proton exchange membrane fuel cell one of the main component is the proton exchange membrane. Per fluorinated membrane (nafion) were commercialized for the proton exchange membrane which have the disadvantages of high cost ,where nonfluorinated polymer membrane have the advantages of lowcost,high thermal stability and the main disadvantages of per fluorinated polymer is swelling property[1-4].Polymer matrix membrane can increase the properties such as mechanical strength, thermal stability and good flexibility[4].

The alternative materials such as Polyvinyl alcohol(PVA) with metal oxide (GO) have been used as a membrane for PEMFC.[5]PVA is one of the polymer which have the good mechanical property, thermal property ,low cost, good chemical resistance[6-7]. Polyvinyl alcohol is the hydrophilic nature polymer which have the OH group that relates the chemical cross linking in acidic conditions and also it have the good water uptake, good tensile strength [8-10].PVA is chosen for the proton exchange membrane because it is non-toxic, water soluble and it is not expensive[11]. Graphene is a 2Dimension layer which consists of $sp^2$ hybridized carbon which has the singe atom and it has the excellent mechanical stability [12]. Graphene is widely used in many applications namely energy conversion ,nanoelecrtonics, sensors and storage materials [13-16]new carbon based nanoscale material Graphene oxide(GO) which have the oxygen functional groups[17-18]. And it consists of both hydrophilic and hydrophobic nature which tends to be unique properties [19-20]. GO is used to produce the thin membranes to reduce the pore size and the membrane flue [21-23].The incorporation of GO in PVA which enables the high surface ratio, high mechanical strength and it provide a more proton transport channels which improve the proton conductivity of the membrane [24].the Sulfonated groups enhance the interface between polymer and Graphene oxide and it enables stronger H- bonding with $SO_3H$ group. The strong H-Bonding interaction with the OH group of PVA give the stronger structure for the

membrane [25-26].the composite membrane SGO/PVA can be operate in high temperature with low humidity[27] in PEMFC Electrospun is one of the method to produce nanofibers from micro to nanometer range. It is the attractive method for producing nanofibers from the polymeric solutions because it have the high productivity, low cost and simplicity [28-29].

The large surface area to volume ratio of the nanofibers are very attractive in the membrane process and it employed that the proton exchange membrane with the improved proton conductivity and lower water swelling property.[30-32]. In this present paper we reported that the comparison between GO/PVA and SGO/PVA on the use of electro spinning method to produce fine nanofibers for proton exchange membrane and it investigate through Scanning Electron Microscope (SEM), X-ray Diffraction Analysis(XRD) and Fourier Transform Infrared Spectroscopy(FTIR).

## 2. EXPERIMENTAL SECTION

**Materials:**

PVA (Polyvinyl Alcohol) [MW=13000-23000] was purchased from the Central Drug House Pvt. Ltd, Graphite fine powder with Extra purity 98% ,Sodium nitrate ($NaNo_3$), Potassium permanganate($KMNO_4$) [MW=158.03],, Hydrogen Peroxide($H_2SO_4$), Sulphuric acid and hydrochloric acid($H_2O_2$) were purchased LOBA chemicals Pvt. Ltd. and all the materials were used without any further purification

**Synthesis of Graphene Oxide (GO):**

2 g of Graphene powder and 2 g of Sodium nitrate ($NaNo_3$) were mixed in 50 ml of Hydrogen Peroxide ($H_2SO_4$) in a beaker under ice bath (0-5$^0$ C) with continuous stirring. The mixture was stirred for 2 hrs after that 6g of Pottasium Permanganate were added to that suspension slowly. Then ice bath were removed and mixture were stirred at 35$^0$ C until it become the brownish color. 100 ml of Distilled water were added in the mixture and increased the temperature to 98$^0$ C. Further the solution was treated by 200 ml of water and stirred continuously. Finally the solution was treated with 10 ml of Hydrogen Peroxide ($H_2O_2$) and it became yellow color. And the solution were washed and centrifugation with 10% Hydrochloric Acid and deionized water several times. After that the solution were filtered and dried at the vaccum temperature then Graphene oxide (GO) is obtained.

**Synthesis of Sulfonated Graphene Oxide (SGO):**

2 g of graphite powder were mixed in 50 ml of sulphuric acid and phosphoric acid. The mixture was stirred continuously for 2 hrs. and 6 g of potassium permanganate were added in the solution at the temperature 35$^0$ C for 12 hrs stirring. Then the solution was treated with 500 ml of distilled water and adds 2 ml of hydrogen peroxide were added. Further the solution were wased and filtered then dried the mixture at a vaccum temperature. Sulfonated Graphene oxide (SGO) was obtained.

**Preparation of Composite membrane:**

2 g of PVA were mixed with 25 ml of distilled water and stirred at 80 $^0$C temperature for 1 hr until it become homogeneous. Then 0.5 g of GO/SGO was mixed with the PVA solution separately and ultrasonicate the solution for 1 hr. The composite solution were loaded in the syringe with a needle tip 25mm gauge and it connected to the DC high voltage .Aluminum foil is placed 10 cm before the needle tip was served as a collector. The voltage applied was maintained to 15-20 kV. The solution were deposited and collected as nanofibers by electro spinning.

## 3. CHARACTERIZATION

All specimens are tested under flexural loading on universal testing machine (UTM). The deflection at center of beams is recorded for each specimen. The observed deflections are used for finding modulus of elasticity of each specimens. It is observed that all the specimens are fail in shear.

**SEM:** The morphology of the composite fiber were characterized Scanning Electron Microscopy (SEM)

**XRD:** An X- ray diffraction was used to obtain the crystallinity of the composite membrane. The radiation was passed using Cu at an operating power 40 kV.

**FT- IR**: An FTIR characterization was performed using a Spectrum 400 FT-IR/ FT-NIR Spectrometer (PerkinElmer). The wavelength range was set from 4,000 to 400 cm-1 to allow for analysis of the functional groups of the nanofibers.

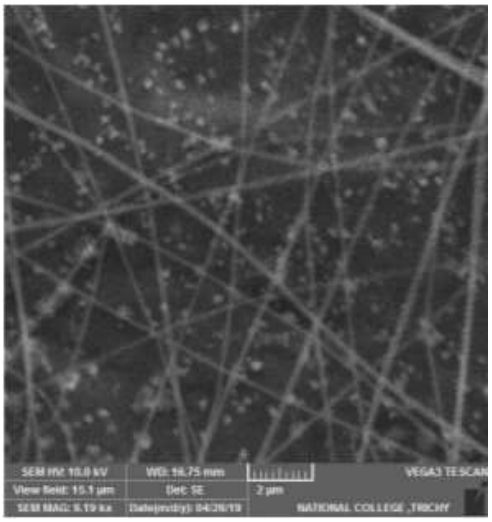

**Fig.1. SEM image of electrospun PVA/SGO**

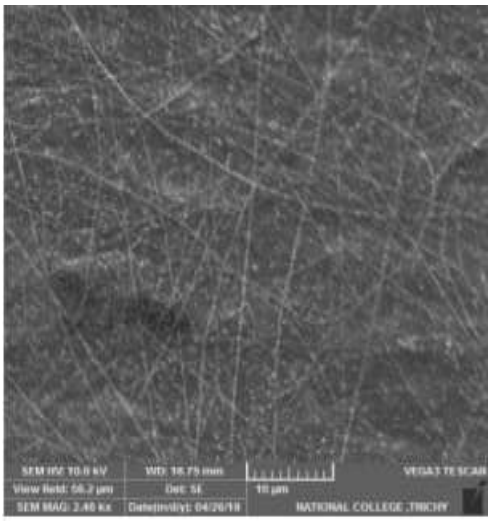

**Fig.2. SEM image of PVA/GO at 2 µm**

Fig.1. shows that the morphology of the prepare composite membrane. The electro spinning process were to remove the water from the from the solid PVA/GO/SGO nanofibers. It is clearly shows that the SEM image which are uniform in diameter and the surface morphology with a diameter (a) 10 µm µm and (b) shows 2 µm. that is 200 nm The image demonstrate that the GO experiments and the parameters obtained were almost gives the nanofibers indicating the choice of spinning method is right

**X RAY DIFFRACTION (XRD)**

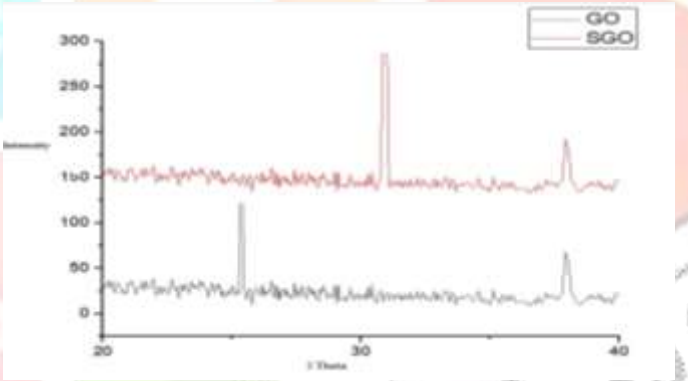


**Fig.3. XRD peak for GO/PVA,SGO/PVA nanofiber**

The XRD spectra of the GO/PVA nanofibers expose only the diffraction peak originating from PVA. Graph.3. shows that the broad peak of GO/PVA $2^{\theta}$ =27˚. These results suggest that GO nanosheets were uniformly distributed in the PVA solution, and the crystalline structure of PVA was influenced by the addition of GO.
The SGO/PVA broad peak which shows at the $2^{\theta}$= 32˚ results that the fibers which are agglomerated with another material but the materials are strong and brittle.

**FTIR (FOURIER TRANSFORM AND INFRARED SPECTROSCOPY):**

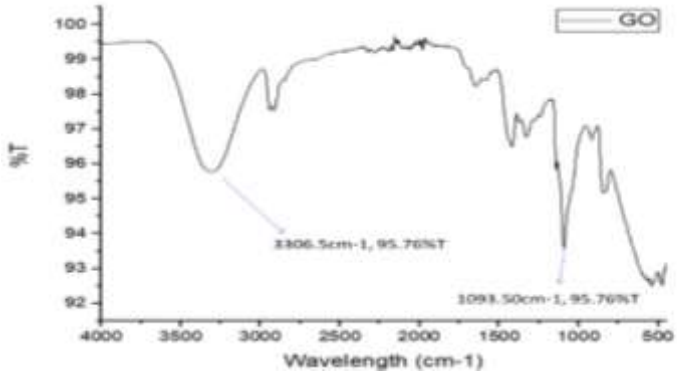


**Fig.4. FTIR Spectra of PVA/GO nanofiber**

The prepared PVA/GO composite nanofiber indicates that the GO functional groups are present in the FTIR spectra. The Fig .4. Illustrates the peak of FTIR spectra that lie in 3306cm$^{-1}$,1093cm$^{-1}$ C-H aliphatic bending, and stretching vibration of C- C at the backbone polymer. The changes of the peak are due to the hydrogen bonding that it exists between the polymers PVA and GO composite.

**THICKNESS OF THE NANOFIBERS:**

| Membrane | Thickness (mm) |
|---|---|
| GO/PVA | 0.025 |
| SGO/PVA | 0.020 |

**Table.1. Thickness of the nanofibers**

The fiber diameter increased with increasing the concentration of polymer and the nanocomposites significant variation of the membrane due to the spinning time and the distance between the syringe and the collector.

## 4. CONCLUSION

Novel SGO/PVA and GO/PVA nanofibers were successfully prepared by electro spinning method. The high content of SGO and GO are uniformly dispersed in PVA to form PVA/GO nanofibers. The SEM shows the morphology structure of fibers at 200 nm. The XRD image shows that the nanofibers are crystalline in nature and the GO, SGO materials have the relatively high purity. The FTIR spectrum exhibits the stretching vibration of aliphatic groups, carboxyl groups that shows the high interaction of the composite material. These results demonstrate that SGO/PVA, GO/PVA nanofibers are efficient, and it has the high strength, reliability and ductility which can give the high performance in proton exchange membrane. Better the SGO/PVA results can be more efficient than GO/PVA due the sulfuric groups present in that. Sulfuric group's helps to conduct more number of proton than any other material thus, the SGO/PVA can gives the more efficient for proton conduction in fuel cells.

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