Synthesis of Phosphorylated Poly(Vinyl Alcohol) and Sulphonated Graphene Oxide Membrane Applied in MFC for Power Generation and COD Removal

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Abstract ***In this study, the partially PPVA and SGO membrane was prepared which was characterized by chemical, structural and thermal properties. Evaluated properties showed good proton conductivity(PC), Ion exchange capacity(IEC)and higher water uptake. The prepared membrane was employed in dual chamber microbial fuel cell (MFC). By calculating the production voltage and the reduction rate of COD the performance of MFC was studied where the results showed power density of 561.1 mW/m2 and COD removal of 78.8% which implies its application in an electrochemical device.***

Keywords: PPVA-SGO, MFC, COD removal

I. INTRODUCTION

Microbial Fuel Cell (MFC) is amongst the best technology where it is an bioelectrochemical device which is useful for converting chemical energies to electrical energies with the help of microorganisms for energy production and wastewater treatment. [1,2]In this research, an dual-chamber MFC is used where prepared proton exchange membrane (PEM) is positioned in the middle ofthe partition of these two compartments for allowance of the protons to pass from anode to cathode chamber.[3] Various PEM are used nowadays but due to high cost and low stability under certain conditions shows limited applications, thus oraganic-inorganic composites of polymer are in much demand which could provide better mechanical and thermal stability. [4] Graphene oxide (GO) is the most promising nanomaterials, which is used for preparing unique membranes[5].Moreover, the thickness of the GOmembrane can be simplyaccustomed by various GO layers [6,7]

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Polyvinyl alcohol is vital polymers as it have worthy mechanical and thermal properties. It also provides nice chemical resistance, film developing ability, and available at low cost. [8,9]It also provides good tensile strength, water uptake and flexibility. In this research, aninnovativeapproach for fabrication ofPEM using Phosphorylated PVA and sulfonated graphene oxide (SGO) was stated. The PPVA solution was dispersed with SGO and the achieved mixturewasused to fabricatethe thin film membraneby solution casting method. This researchdisplayscross-linksforenhancing theproperties like chemical bonds, thermaland mechanical stabilities of membrane, this is achieved due to functionalizing both, organic andinorganic compounds.

II. MATERIALS

Polyvinyl alcohol (PVA) and Phosphoric acid (0.1-0.5M) for phosphorylation. 25% aq. Solution of Glutaraldehyde and 97% of chlorosulfonic acid for sulfonation. Graphene oxide (GO), phosphoric acid, hydrogen peroxide, sulphuric acid, methanol, NaCl etc. of AR grade and used with suitable purification. The milli-Q water in all experiments was used.

III. METHODOLOGY

Partly phosphorylated polyvinyl alcohol (PPVA)isachievedby a mix of Polyvinyl alcohol (6.6 g), phosphoric acid (PA) of 0.1–0.6 M and water (25 mL). In the meantime, with constant stirring at 80°C the refluxing process was carried out. The GO from natural graphite was made by the modifiedHummer's process.[10]This synthesized graphene oxide was improved according to the stated method for preparation of SGOwithsulfanilic acid aryl diazonium salt.[11]. This mechanism comprises the homolytic division of dinitrogen from the diazonium salt thus leads to the formation of aryl radical whichfixes to the graphene surface via C–C covalent bond.[12]. The prepared SGO was dipersed in PPVA mixture with continuous stiring and slighlty heating. The membrane was then prepared by catsing method on round plate and vacuum dried for 24 hrs.

For sludge preparation 200 mL of anaerobic sludge was injected in the anode chamber[13]with 2 g/L glucose having 2000mg/L COD the medium was prepared of pH 6.8 to 7.2. Potassium permanganate ($KMnO_4$) of

0.2 g/L concentration was added to the cathodic chamber for enhancing the decline of H+ ions [14]

IV. RESULTS AND DISCUSSION

A. Ion-exchange capacity (IEC)

For prepared membrane the IEC evaluated is mentioned in Table 1. The acidic groups like sulphuric acid $-SO_3H$ and phosphoric acid $–PO_3H_2$ boosts proton conductivity and thus the increase in the IEC of the membrane [15]

Table 1: Evaluated properties of prepared PPVA-SGO membrane water uptake , Swelling area and IEC

Membrane	Water uptake, %	Swelling Area %	IEC
PPVA-SGO	124	59.5	1.86 meq/g

B. Water uptake and swellingdegree

Water shows a chief role in proton conductionin PEMs as it permits the transfer of proton by giving proton medium, creating networks of hydrogen-bond, and separating conducting groups. However, additional water uptake may decay its mechanical stability, and its performance. The water uptake determined for PPVA-SGO was 124% this could be due to the presence of acidic groups of sulphuric acid $–SO_3H$ and phosphoric acid $–PO_3H_2$ as both have higher attraction towards the hydration. As higher water uptake will show higher area swelling thus for PPVA-SGO membrane showed 59.5% of swelling degree mentioned in Table 1.

C. *Proton conductivity*

For studying the performance measuring proton conductivity at 27^{o}C and 50^{o}C with relative humidity of 50% of synthesized PPVA-SGO membrane by EIS was done. The proton conductivities of synthesized PPVA-SGO membrane are stated in Table. 2. The presence of acidic groups - SO_3H and $–PO_3H_2$ was responsible for transfer of proton [16-18].

Table 2: Evaluated Proton Conductivity (PC) in S/cm of PPVA-SGO membrane at 50% relative humidity

Membrane	PC at 27 ^{0}C	PC at 50 ^{0}C
PPVA-SGO	9.8 x 10-2	13.4 x 10-2

D. Thermo-gravimetric analysis (TGA)

The prepared membrane was inspected for the thermal stability with a 100 C/min heating rate under dry air by TGA. The thermograph of PPVA-SGO membrane is presented in Figure 1. The membrane was found to be stable thermally up to 220^{o}C. Several weight loss steps are analyzed in the TGA graph. Thewater absorbed by the membrane causes better strength of membrane and also due to link with acidic groups of $-SO_3H$ and $–PO_3H_2$.

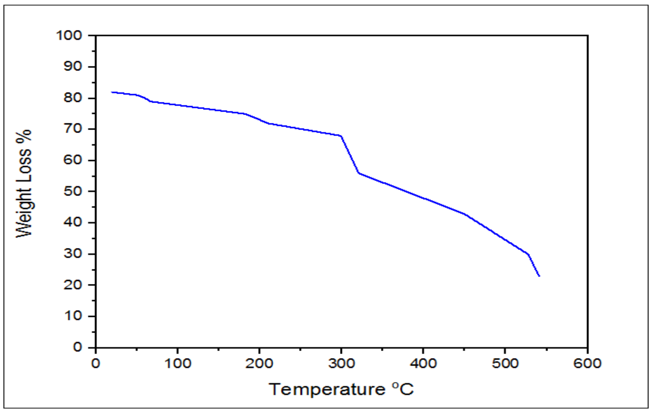

Figure 1: TGA curve for PPVA-SGO membrane

E. Scanning electron microscope (SEM)

By conducting SEM analysis the morphological structure of PPVA-SGO membrane was characterized as presented in Figure. 2. The membrane was found to be blackish in color.Scanning electron microscope image exposed black spots on the surface due to the phosphonic acid impregnation into membrane.

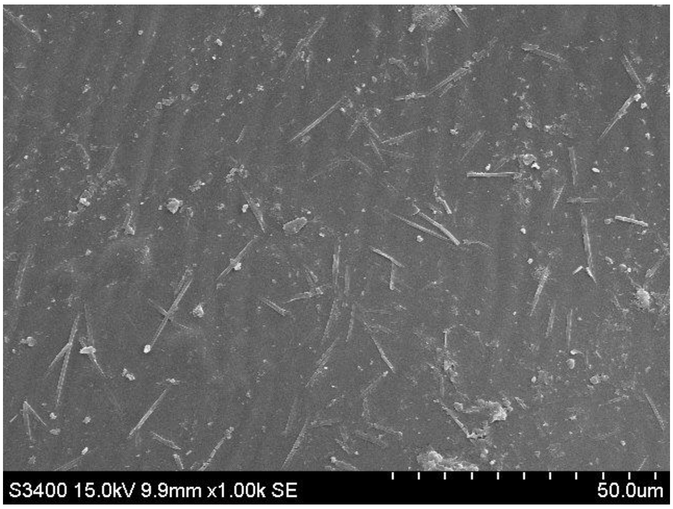

Figure 2: SEM Image for PPVA-SGO membrane

F. XRD

In this XRD technique the resultantcrystal-like, the chain packing and events of the membranes was tested shown in Figure 3. A peak for GO was observed at 9.80^o (2θ) with an basal spacing of 0.89 nm. The d-value evaluated for membrane was 0.45 and 0.39 nm for the sulfonated peaks in the range 2θ= 2 to 15^o.

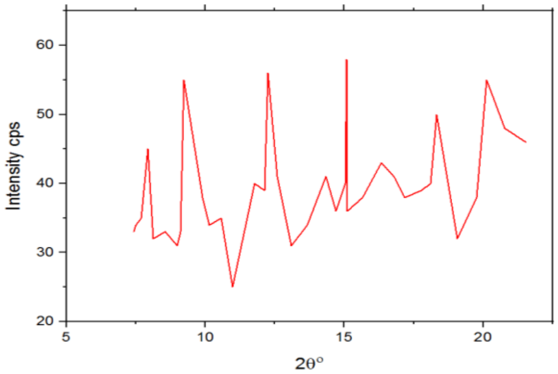

Figure 3. XRD curve for PPVA-SGO membrane

G. *MFC performance*:

For power generation the performance of MFC was considered. The obtained polarization curve for prepared membrane is presented in Figure 4. The extreme power density produced for synthesized PPVA-SGO membrane was found to be 561.1 mW/m^2 for 200 Ω. In anode compartment due to the degradation of organics the protons and electrons are formed. The 2000 mg/L initial COD in anode chamber of substrate and at the end of MFC experiment was 78.8% COD reduction was noted. This is recognized due to the H^+ transport across PPVA-SGO membrane and even enhancement in water uptake and IEC.

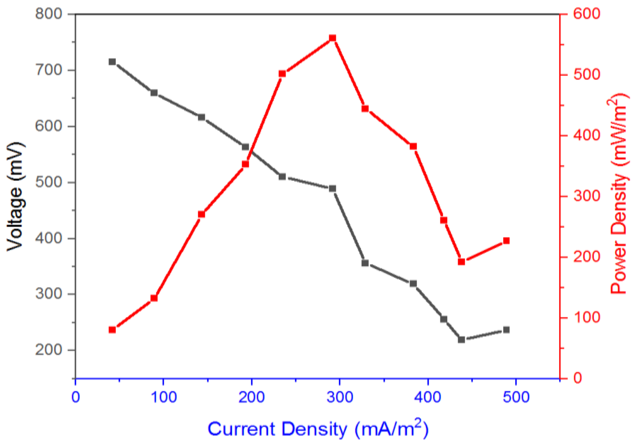

Figure 4:Polarization Curve for PPVA-SGO membrane

V. CONCLUSION

The use of synthesized PPVA-SGO membrane for producing power was achievable in MFCs. The synthesized PPVA-SGO membrane demonstrates the enhanced efficiency due to addition of acidic groups - SO_3H and –PO_3H_2. This enhancement performance is studied by properties like conductivity of proton, IEC, swelling degree, water uptake and thermal strength. For MFC efficiencythe detected the power density was 561.1mW/m^2.Also the study shows higher COD deduction of 78.8%. Herein, all the assessed results of PPVA-SGO membrane prove it's the uses in electrochemical devices. On the other handextra research is essential for commercializing the PPVA-SGO membranes.

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