

Fabrication of Cation Exchange Membrane for Microbial Fuel Cells



Snehal Dawkhar, Salim Attar, Satish Rikame

Abstract: In this study the cation exchange membranes (CEM) were fabricated using 3 different compositions of sulphonated poly vinyl alcohol (SPVA) and phosphorylated graphene oxide (PGO) in weight ratios by physical mixing and casting method. Loading of PGO in the SPVA improved water uptake property which signifies increase in ion exchange capacity (IEC) and proton conductivity as presence of acidic groups were characterized. These fabricated membranes performances were assessed in microbial fuel cells (MFCs) and characterized using XRD and FTIR for its compositional analysis. Due to proper proton conducting channels most suitable CEM (SPVA-PGO-3) revealed higher proton conductivity 9.0×10^{-2} S/cm at 27°C, water uptake 114%, area swelling 54.2% and ion exchange capacity (IEC) 1.92 meq/g. The power density obtained for this composite membrane applied in MFC-3 was observed to be 503.1 mW/m² while the COD removal results obtained as 80.8 %.

Keywords: CEM, COD removal, MFC, SPVA-PGO,

I. INTRODUCTION

Nowadays, application of Microbial fuel cell (MFC) is increased in power generation, as it is green method utilizing wastewater for microbial oxidation of present organic impurities. [1]. Thus materials with high water retention are required to be identified and used in MFCs to attain good performance and extended lifespan without any wear caused by dehydration. Recently, remarkable efforts were taken via physical or chemical modifications for improving the water retention even by incorporating the hydrophilic fillers of PEM [2]-[6]. For improving the water uptake different inorganics are used as they offer sites of hydrogen-bonds and hydrophilic fields. [7]-[9] However, addition of graphene oxide (GO) as organic filler was found to be best as its combination improved proton conductivity and water retention. [10], [11] Noteworthy efforts for fuel cells were taken for improving its efficiency, stability and cost using graphene. [12]-[15] It was recognized that proton conductivity might be enhanced by grafting of $-PO_3H_2$ group on GO

. Perfluorosulfonic acid PEMs (Nafion), is used as reference membrane fuel cell (MFC) because of its electrochemical properties and chemical stability. [16]-[19] On the other hand, performance of Nafion above 80°C is less which is a serious concern thus research is on verge for addition of multifunctional fillers for better PEM. Polyvinyl alcohol (PVA) is a hydroxyl rich, biocompatible, non-toxic, and water-soluble

system, which is treated by aqueous methods.

It is a significant polymer having several uses in membrane technology [20] and fuel cells [21]. The improved properties of the PVA membranes are accomplished by inorganic additive ($-HSO_3$) blending [22][23]. For studying the strengthening behaviour of GO fillers, polymer matrix of PVA is preferred. The composite PEM grafted with $-HSO_3$ and $-PO_3H_2$ multifunctional clusters and preferred level of cross linking estimated to exhibit good proton conductivity.

In this manuscript, the synthesis of PEM was done using water-soluble polymers with varying weight ratios. Polymers such as PVA were used to enhance the water passage due to their properties like hydrophilic in nature. [24] Phosphoric acid, has particular properties, like exceptional stability in fuel cell applications in terms of thermal, chemical and electrochemical. The fused PEMs characterized by using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) for its compositional analysis. The water uptake, proton conductivity and ion exchange capacity of the fused membranes were calculated. The fused membranes were used in different MFC setups and its efficiency was supervised in regard to open circuit voltage (OCV), power and current density, and related with the Nafion 117 membrane. Chemical oxygen demand (COD) removal of wastewater was also determined.

II. MATERIALS

Polyvinyl alcohol (PVA), 125000 avg molecular weight, 99% pure from Sigma Aldrich while Graphene oxide (GO) prepared from Graphite powder of 100 μm size, from SD fine chemicals India, for sulfonation 25% aq. Glutaraldehyde and 97% chlorosulfonic acid (Analytical grade) and 3-aminopropyltrimethoxysilane (APTMS) was used as obtained from Sigma Aldrich chemicals. All chemicals from SD fine chemicals India were obtained and used with appropriate refining. Tetrahydrofuran (THF), acetone, HCHO, acetic acid, H_3PO_4 , HCl, H_2O_2 , H_2SO_4 , NaOH, $KMnO_4$, methanol, NaCl etc. were used. In all experiments, distilled water was obtained and used.

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III. METHODS

A. Sulfonation of PVA (SPVA)

The process followed for sulphonation is, 90 mL distilled water was taken with 10 gm, 20 gm and 30 gm PVA dissolved respectively with continuous stirring. This solution was heated for 1 hour at 50°C. The aqueous mixture formed was sulfonated with chlorosulfonic acid 1 mL, 2 mL and 3 mL respectively and later glutaraldehyde 0.5 mL was added for cross linking. The obtained sulfonated solutions of PVA was cooled to for 2-3 hour 15°C.[25]

B. Preparation of graphene oxide

Following Hummers method for GO preparation, 2.0 gm flakes of graphite and 2.0 g sodium nitrate were added in a round bottom flask to H₂SO₄ (90 mL) positioned in an ice bath with continuous stirring. KMnO₄ (6.0 g) was steadily added with stirring at a temperature >20°C and then the temperature for 1 h was increased to 35°C. Finally, to neutralize the excess amount of permanganate 30% of H₂O₂ was added. The gained mixture was centrifuged, and the precipitate was splashed with HCl(aq) and water and then dried for overnight under vacuum.

C. Synthesis of N, N-dimethylene phosphonic acid propyl silane graphene oxide (NMPSGO)

By a condensation reaction between APTMOS and GO the Aminopropylsilane graphene oxide (APSGO) was prepared. In a typical procedure, anhydrous THF (500 ml) and oxygenated GO (50 mg) was stirred and sonicated for obtaining a stable dispersion mixture. Then, 0.5 ml APTMOS was added to the mixture and then this mixture for 15 hours was refluxed. The reaction mix obtained was brought to normal room temperature, which was then filtered and bathed numerous times by THF, and vacuum dried [26].APSGO obtained was then distributed in a closed vessel containing formaldehyde and phosphorous acid solution (1:1 (w/w)) and stirred at 70°C for 3 hours. After cooling the mixture to normal temperature, filtration was done. The obtained NMPSGO was water washed, and then vacuum dried.

D. SPVA-PGO

In different ratios, the above mixture of PGO (0-8%) was dispersed in prepared SPVA solutions with continuous stirring and slight heating. The obtained viscous solutions of composite membranes was casted on 3 different glass plates. These casted membranes was then dried for nearly 7 hours at a temperature of 50°C. the prepared membranes were named as M1, M2 and M3.

IV. MEMBRANE CHARACTERIZATION

The prepared membrane was characterized by FTIR, while by the titration method Ion Exchange Capacity (IEC) was measured; where for replacement of all protons with Na⁺ ions NaCl (2.5 M) solution was used to saturate the membranes for about 15 hours. For neutralizing the protons the solution was titrated against NaOH (0.05 M) using indicator phenolphthalein, using formula [27] the IEC (meq/g) was evaluated by

$$IEC = \frac{AXB}{m} \text{----- (1)}$$

Where ‘A’ (mL) is volume of titrant at the equivalent; ‘B’ titrant molar concentration and ‘m’ dry membrane weight

(0.1652 gm).X-ray diffraction was used to spot the molecular filler of the membrane of Rigaku, Model D, using radiation CuK α operating at 30 mA and 40 kV with 5 min⁻¹ scanning rate and 0.041 of 2 θ angular resolution. The Scanning Electron Microscope (SEM) spectroscopy analysis of membrane was done by S3400 with 220 kV acceleration voltages. The Water uptake was evaluated by measuring the dry and wet membrane weight. A rectangular-sized dry membranes was soaked for 24 hours in deionized water. In order to get rid of the surface droplets the membrane was then dabbed with paper and then the re-measurement of size and weight was done. This procedure was done for 3 times with an error range of \pm 5%.

For measuring the Water uptake succeeding equation [25] was used:

$$WaterUptake = \frac{(W2 - W1)}{W1} \times 100 \text{----- (2)}$$

Where W1, the dry membrane initial weight of and W2, the hydrated membrane final weight.

By using the EIS the proton conductivity was estimated [28]. The following equation used for calculating the conductivity:

$$\sigma = \frac{L}{RXa} \text{----- (4)}$$

Where σ is the conductivity (S/cm), L (cm) the membrane thickness, a (cm²) the electrode area and R (Ω) the across the membrane resistance.

V. MFCCONSTRUCTION

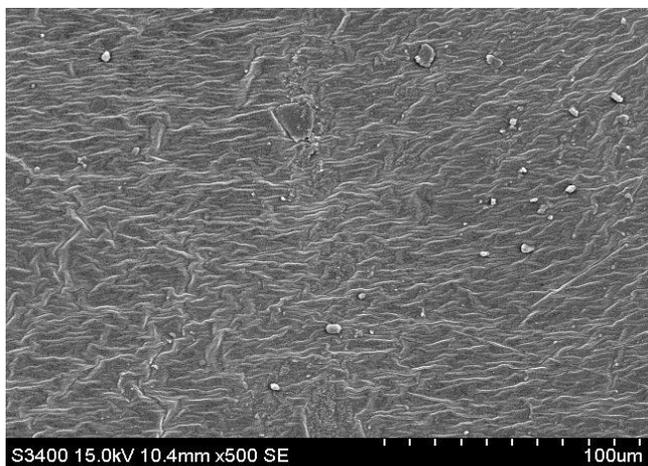
Dual chambered microbial fuel cell (Lab scale) was fabricated for this batch study. The two chambers made of polyacrylic material of 1.2-liter capacity each, with dimensions of each compartment 13 cm (height), 10 cm (length) and 10 cm (width). The working volume was 1 lit. The chambers were linked by a flange, in which the proton exchange membrane was assembled. To avoid leakages rubber gaskets and silicone gel for binding the gaskets were used. In anode and cathode chambers the flat plate of pure carbon of 9 x 1.5 cm (length x width) were used as electrodes. The 13.5 cm² was effective surface area of the electrode, for avoiding high contact resistance these electrodes were drilled and soldered for connecting copper wires. For anaerobic treatment the anodic chamber was closed with an airtight lid, while the cathodic chamber was left open to the atmosphere. The effective diameter was 2.5 cm of a membrane connecting the two chambers. Both chambers were parted by PEM for setups MFC1, MFC2, MFC3 with prepared different compositions of SPVA-PGO as M1, M2 and M3 and MFC4 with Nafion-117 membrane as reference and all conditions for all the sets were maintained same. From sewage plant, 200 mL anaerobic sludge was inoculated in the anode chamber [29], [30] with glucose 2 g/L having 2016mg/L COD the medium was prepared. The pH of the medium was 6.8 to 7.2. At 30 \pm 1°C temperature MFCs were maintained. As an electron acceptor the O₂ was continuously supplied in cathode chambers.

Potassium permanganate (KMnO_4) of 0.2 g/L concentration was added to the cathodic chamber for enhancing the decline of H^+ ions [31]. The preliminary pH of KMnO_4 solution was 7.3 which were kept at 7 throughout the study, by addition of few drops of 0.5 M H_2SO_4 or 1M NaOH, as/if required [32].

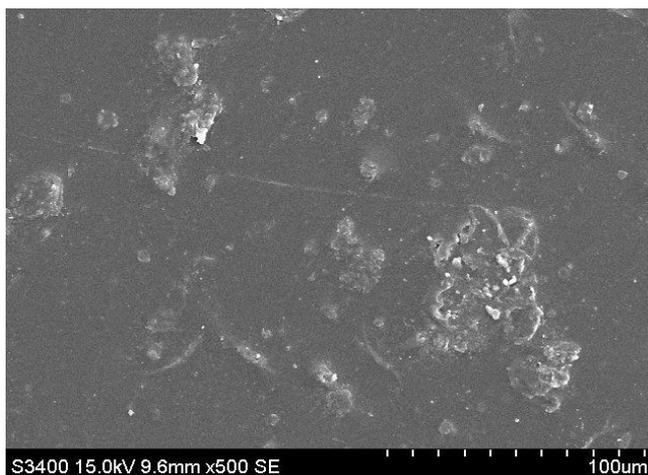
VI. RESULTS AND DISCUSSION

A. Scanning electron microscope (SEM)

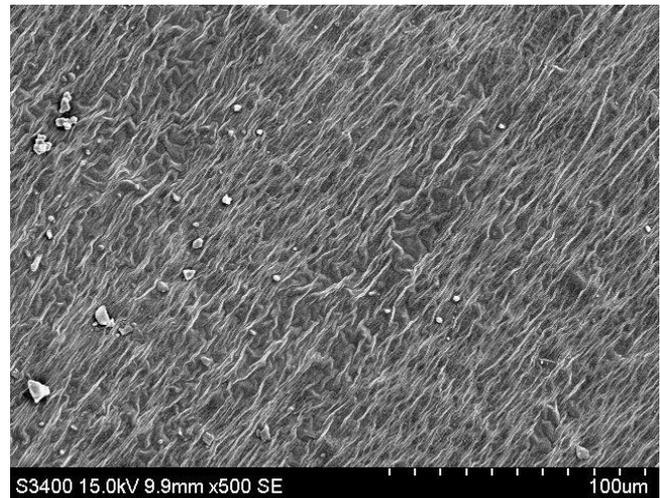
By SEM analysis the morphological structures of surface of SPVA-PGO membranes was characterized as presented in Fig.1a, 1b and 1c. The prepared SPVA-PGO membranes were light blackish in color and transparent. Scanning electron microscope image exposed relatively flat, exfoliated with lined structure, while black spots on the exterior due to the phosphonic acid impregnation into membrane. Due to the PVA sulfonation the cavities may be present which could be the apparent cause for the increase in water uptake of SPVA-PGO than Nafion-117.



a. Membrane 1 SEM image (M1)



b. Membrane 2 SEM image (M2)



c. Membrane 3 SEM image (M3)

Fig. 1. SEM images of prepared membranes

B. FTIR of SPVA-PGO

The prepared membrane composite FT-IR spectra are shown in Fig. 2. The peak at 1328.95 cm^{-1} corresponds to the phosphonic acid stretching vibration; the presence of $-\text{PO}_3\text{H}$ is confirmed by P=O groups. The amplified intensity at 2924 cm^{-1} and 2854 cm^{-1} of the C-H bands corresponds to stretch vibrations of the methylene group, specifies the reduction of graphene-COOH to hydroxymethylene group. The strong peak of P-O-H group vibration stretching observed at 3234.62 cm^{-1} while at 3361.93 cm^{-1} a strong and broad absorption due to O-H extending vibration was observed. Absorption band 1680 cm^{-1} carbonyl extending and 1438.90 cm^{-1} a frail absorption band of OH stretching -COOH group. At 1174.65 cm^{-1} strong absorption band detected due to the C-O stretch of cyclic ether rings, confirming the membrane matrix cross-linked structure. After sulfonation of PVA peaks at 1134.14 cm^{-1} and 1093 cm^{-1} , confirms the sulfonic acid existence while 997.20 cm^{-1} shows presence of $-\text{SO}_3\text{H}$ group stretching vibration. The peak at 844.82 cm^{-1} indicates p-disubstituted phenyl group characteristic vibrations and the P-O bending vibration band at 491.85 cm^{-1} appears in the spectrum of PGO. This way, FT-IR confirms grafting of $-\text{SO}_3\text{H}$ and $-\text{PO}_3\text{H}_2$ acidic group into the composite prepared membrane.

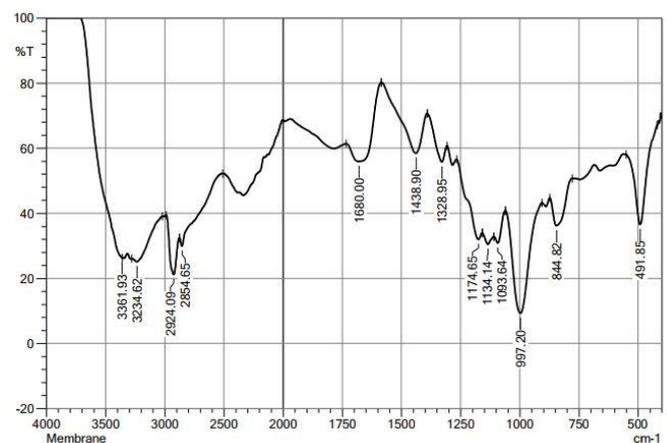


Fig. 2. FTIR Curve for SPVA-PGO

C. XRD

By XRD technique the resulting crystalline, the chain packing and activities of the membranes was tested shown in Fig. 3. Diffraction peak for GO was observed at 9.80° (2θ) basal spacing (0.89 nm), which was shifted at 2θ=20° for APSGO. The d-value for membranes was 0.45 and 0.39 nm evaluated for the sulfonated PVA peaks in the range 2θ= 2 to 15°.

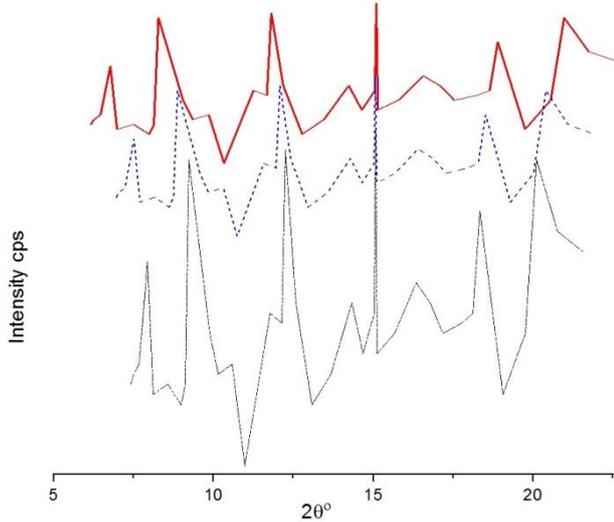


Fig.. 3 XRD analysis

D. Ion exchange capacity (IEC) and Proton conductivity

The acidic groups -SO₃H and -PO₃H₂ shows enhancement in proton conductivity and in result the IEC of the membrane [33].The IEC calculated was found to be 4-5 times higher of prepared SPVA-PGO membrane with higher PVA content. Table 1 demonstrates the IEC values for prepared SPVA-PGO membranes. The proton conductivity and IEC are directly relative to each other [34]. More solvated species should be produced for high proton conductivity with high water content for membranes [35]. To demonstrate the performance by determining proton conductivity at 27°C and 50°C with relative humidity of 50% of prepared SPVA-PGO membranes by EIS was done. The proton conductivities of prepared SPVA-PGO membranes are stated in Table. 1. The proton conductivity 10.60 x 10⁻² S/cm at 27°C and 13.8 x 10⁻² at 50°C of SPVA-PGO membrane was found best.

Membrane	IEC meq g ⁻¹	Proton conductivity (temp 27°C) for 50% RH (S/cm)	Proton conductivity (temp 50°C) for 50% RH (S/cm)
M 1	1.69	8.70 x 10 ⁻²	9.30 x 10 ⁻²
M 2	1.72	9.1 x 10 ⁻²	12.7 x 10 ⁻²
M 3	1.96	10.60 x 10 ⁻²	13.8 x 10 ⁻²
Nafion-117	0.92	7.40 x 10 ⁻²	-----

E. Water uptake

In PEMs it is well recognized that water plays a crucial role in proton conduction as it enables the transfer of proton by providing proton medium, creating hydrogen-bonded networks, and separating conducting groups. The water uptake determined for prepared SPVA-PGO membranes were 108%, 118% and 124% respectively while for Nafion-

117 was 27%. This shows M 3 has high water uptake than Nafion-117 and other synthesized membranes due to the existence of acidic groups of -SO₃H and phosphoric group -PO₃H₂ in SPVA-PGO membranes as both -SO₃H and -PO₃H₂ groups shows higher affinity towards the hydration.

F. MFC Performance

For power generation the performance of MFC was studied. The obtained polarization curve is presented in Fig.4 and Fig. 5. The polarization curve depicts plots for prepared SPVA-PGO membranes. The extreme power density produced for SPVA-PGO (set 3) was for M1 : 552.4 mW/m², 502.1 mW/m² SPVA-PGO (set 1) 497.6 mW/m² for SPVA-PGO (set 1). Table 2 shows the performance summary of the prepared SPVA-PGO membranes

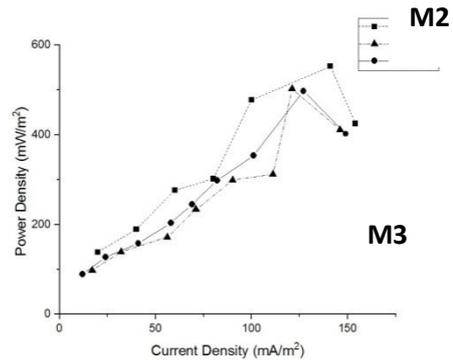


Fig.4. Power density curve for synthesized membranes in MFCs setups.

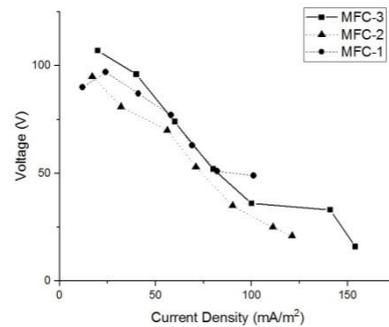


Fig. 5 Polarization curves of the synthesized membranes in MFCs setups.

TABLE 2 Summary of the performance factors of various synthesized membranes in MFCs

MFC	Membrane	Maximum Power density mW/m ²	Maximum Open Circuit Voltage V	COD removal %
MFC 1	M1	497.6	90	80.8
MFC 2	M2	502.1	95	82.8
MFC 3	M3	552.4	105	86

In anode compartment due to the degradation of organics the protons and electrons are formed.

The 2016 mg/L initial COD in anode chamber of substrate and at the end of MFC experiment for set 1 80.8%, set 2 82.8% and set 3 86% COD reduction and 77.3% for Nafion-117 was noted.

VII. CONCLUSION

The use of synthesized SPVA-PGO membranes for generating power was viable in MFCs and signified improved power density. The prepared SPVA-PGO membranes demonstrate the enhanced efficiency over the Nafion-117 membrane due to addition of phosphorylated graphene oxide and sulfonated PVA solution. This enhancement performance is studied by properties like conductivity of proton, IEC, swelling degree, water uptake and thermal strength and compared with commercial Nafion-117. For MFC set 3 using M-3 exhibited the peak performance in terms of the power density (552.4 mW/m²), COD reduction (86%), water uptake, IEC, Proton Conductivity. Likewise the study shows higher COD deduction for set-1 (81.8%). Herein, all the estimated performance results of SPVA-PGO membrane prove it is more effective and efficient due to PVA content.

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