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Efficient electrodes and electrolytes for enhanced performance of proton exchange membrane fuel cells

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Abstract: Efficient anode catalyst for hydrogen oxidation for use in proton exchange membrane fuel cell (PEMFC) was synthesised using suitable precursors for iridium, molybdenum and vanadium with activated carbon as catalyst support. Graphene was synthesized using modified Hummer's method for its application as catalyst support. Graphite oxide and reduced graphene oxide were analyzed using SEM. The catalytic activity was analysed using cyclic voltammetry (CV) and the composition of the elements were analysed using ICP-OES. XRD was used to analyse the crystallinity and particle size of the sample. Composite membrane electrolytes for PEMFC application were fabricated by blending sulfonated polystyrene ethylene butylene polystyrene (SPSEBS) with sulfonated inorganic filler material, silica (SiO_2). The SPSEBS, sulfonated SiO_2 particles and the composite membranes were characterized using FTIR spectroscopy and XRD, which indicated the level of crystallinity. The effects of different proportions of sulfonated SiO_2 in SPSEBS matrix were analyzed for their ion exchange capacity (IEC) and proton conductivity using impedance spectroscopy. Water uptake of the membranes was also examined and the surface morphologies were studied by SEM.

Keywords: Sulfonated polystyrene ethylene butylene polystyrene, Sulfonated silica, Composite membrane, Graphene, Iridium, Vanadium, Molybdenum, PEMFC.

Introduction

The proton exchange membrane fuel cells (PEMFC) offer a perfect stepping stone in the commercialization of fuel cells. They can be operated at low temperatures. They can also be scaled up for larger projects¹. PEM offers a great balance between power and size/operating temperature². A typical catalyst support material used is Vulcan XC72R. Another alternative is to use graphene as a catalyst support due to its robust and flexible characteristics. Graphite oxide (GO) is a hydrophilic derivative of graphene³. GO is produced by Brodie, Hummer or Staudenmeier⁴⁻⁸. GO consists of graphene sheets decorated mostly with epoxide and hydroxyl groups⁹. A cheaper and a non-fluorinated engineering thermoplastic, polystyrene ethylene butylene polystyrene (PSEBS) was sulfonated to SPSEBS for use as electrolyte in PEMFC¹⁰. The effect of molecular weight of the fluorinated polymer of SPEEK/fluorinated polymer blends have been evaluated for low temperature fuel cell applications¹¹. SPEEK blended with poly vinyl alcohol was tested for direct methanol fuel cell (DMFC) applications¹² etc. All these membranes are being evaluated as alternatives to the fluorinated and expensive Nafion membranes. $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$ bulk metallic glass (Pt-BMG) nano wires are used for

methanol and ethanol-oxidation¹³. In the present work, sulfonated SiO₂ was incorporated into SPSEBS to improve mechanical and conduction properties. The fabrication of the composite membranes, synthesis of Ir-V-Mo alloy catalyst and the results of various characterizations are discussed.

Experimental procedure

Materials

Iridium chloride hydrate [IrCl₃.6H₂O], ammonium metavanadate NH₄VO₃ and hexaammonium heptamolybdate tetrahydrate [H₂₄N₆O₂₄Mo₇.4H₂O] were received from Srihari Scientific. PSEBS, graphite powder, silica, ethylene glycol, hydrazine hydrate and other chemicals were obtained from Sigma-Aldrich (USA).

Synthesis of Anode Catalyst

Desired amount of activated carbon, IrCl₃, NH₄VO₃ and H₂₄N₆O₂₄Mo₇.4H₂O were added to ethylene glycol. Then, a 2 M NaOH solution was added to adjust the pH to 12 and refluxed at 120°C for 3 h. The pH of mixture was adjusted to 3 by adding HCl. Complete reduction was carried in a chemical vapour deposition (CVD) chamber under N₂ for 1 h.

Synthesis of Graphite Oxide

Modified Hummer's method was used to obtain graphite oxide. In the process, graphite powder (2 g; 97% purity) and NaNO₃ (1 g) were mixed, then it was put into concentrated H₂SO₄ (96 ml; 98%) with an ice bath with continuous addition of KMnO₄. The mixture turned out to be a brownish colour paste. After the addition of H₂O₂, the diluted brownish colour solution transformed to brilliant yellow which was dried.

Reduction of Graphene Oxide

Graphite oxide (2g) powder was mixed with water and sonicated with hydrazine hydrate. The round bottomed flask was heated over which the reduced graphite oxide gradually precipitated out as a black solid. The product was isolated by filtration and dried.

Sulfonation of Psebs

5g PSEBS was measured and dissolved in chloroform, and the required quantity of tributyl phosphate (moderator) and chlorosulphonic acid (sulfonating agent) was added which was with continuous stirring in an ice bath. The reaction was terminated by methanol, after which it was dried at 55°C overnight.

Sulfonation of SiO₂

The sulfonating agent, sulphuric acid (0.5 M) was added to 1 g of SiO₂ particles. This solution is subjected to ultrasonication for 1 h. The product was obtained by drying the solution at 100°C for 24 h.

Preparation of Composite Membranes

Required weight percentages of SPSEBS and sulfonated SiO₂ (SiO₂-SO₃H) powders were dissolved in THF solvent. The prepared mixture was poured slowly onto the glass dish. The membranes were designated as SPSEBS – SiO₂ - SO₃H 2.5%, SPSEBS – SiO₂ - SO₃H 5.0%, SPSEBS – SiO₂ - SO₃H 7.5% and SPSEBS – SiO₂ - SO₃H 10.0% according to the weight percentage of the filler material.

Ion Exchange Capacity and Water Uptake

Ion exchange capacity (IEC) depends on the number of sulfonic acid groups that are bonded to the membrane. The SPSEBS blend membrane was immersed in saturated potassium chloride solution over night to allow exchange of protons with K⁺ ions. The protons released from the membrane were neutralized by 0.01 mol/L sodium carbonate solution. Phenolphthalein was used as the indicator. The IEC was calculated using the following formula.

$$\text{IEC} = \frac{\text{Titre value (in mL)} \times \text{Normality of the titrant (Na}_2\text{CO}_3)}{\text{Weight of the dry polymer membrane (in grams)}}$$

To measure the water uptake of the membranes, the samples were dried in the oven at 55°C for 12 hours and weighed (W_{dry}). After immersion in the deionised water for 12 hours, the sample membranes were weighed again (W_{wet}). The water uptake capacity was calculated using the formula given below.

$$\text{Wateruptake, } \Delta W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

Cyclic Voltammetry

Electrochemical characterization of the synthesized catalyst was carried out by CV technique. One milligram of the catalyst powder was suspended in 500 μL of ethanol/Nafion solution (50:1 wt.%) and sonicated to prepare the catalyst ink. Then 5 μL of this ink was transferred to a clean Au/Pd electrode. Catalyst materials were tested for the electrochemical hydrogen oxidation reactivity (HOR) by three-electrode system in 0.5 M H_2SO_4 at 25°C. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire as the counter electrode.

Instrumental Characterization

X-ray diffraction (XRD) is a technique that is used to identify the crystalline and amorphous materials. The FTIR spectra of SPSEBS and composite membranes were taken. The membranes were dried and the surface morphology was studied by scanning electron microscopy (SEM). The elemental composition of the catalyst was measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The conductivity of samples (σ) was determined by impedance spectroscopy using the following formula,

$$\sigma = L/RA$$

where, L is the thickness of the membrane in cm, A is the area of the membrane in cm^2 , R is the resistance in Ω and σ is conductivity in S/cm.

Results and Discussion

Iec and Water Uptake

The ion exchange capacity corresponds to the moles of fixed SO_3^- sites per gram of the polymer. From Table 1, it is clear that the IEC values of membranes increased with the increasing amount of $\text{SiO}_2\text{-SO}_3\text{H}$ particles, due to the sulfonated form of the filler added.

Table 1. IEC of composite membranes

Membrane type	IEC (meq g ⁻¹)
SPSEBS	1.653
SPSEBS-SiO ₂ -SO ₃ H 2.5%	1.856
SPSEBS-SiO ₂ -SO ₃ H 5.0%	2.390
SPSEBS-SiO ₂ -SO ₃ H 7.5%	2.946
SPSEBS-SiO ₂ -SO ₃ H 10%	2.169

Water plays a critical role in PEMFC performance. The water uptake of all the composite membranes was found to be higher than the SPSEBS membrane. This can be attributed to the hydrophilic character of the SiO_2 nano particles.

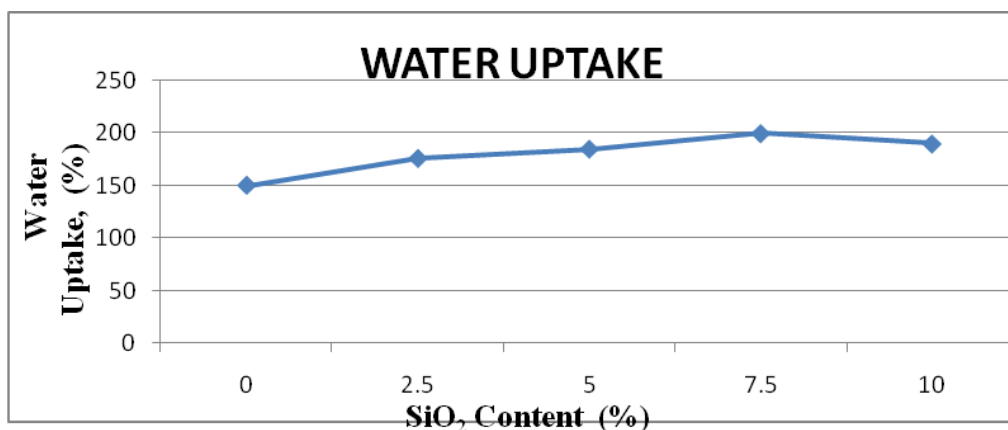


Fig.1 Water uptakes of composite membranes

Cyclic Voltammetry

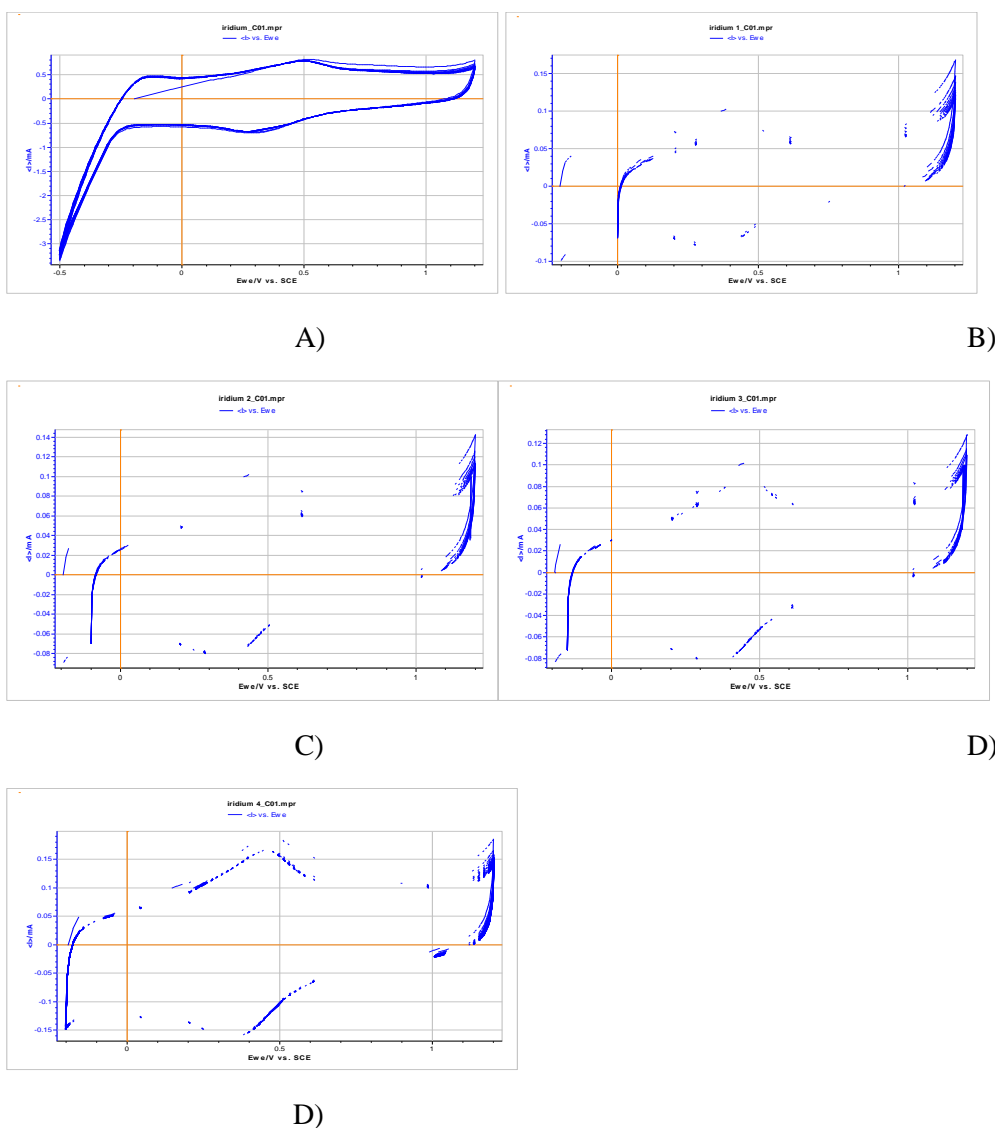


Fig. 2 CV of Ir-V-Mo/C A) scan rate: 5000 mV/s from 1.2 V to -0.5V. B) scan rate: 500 mV/s from 1.2V to 0 V. C) scan rate: 500 mV/s from 1.2 to -0.1 V. D) scan rate: 500 mV/s from 1.2 V to -0.15 V. E) scan rate: 1000 mV/s from 1.2 V to -0.2 V.

Fig.2 shows the CV of 40%Ir-10%V-10%Mo/C at various scan rates. It is evident that the synthesised catalyst oxidises hydrogen and shows as potential replacement for commercial platinum.

XRD

Fig.3 shows the XRD of composite membranes. It is observed from the XRD patterns that there is a slight decrease in crystallinity with addition of SiO_2 particles. The crystallinity decrease is found to be more in the SPSEBS- SiO_2 - SO_3H 7.5% membrane because, beyond this the filler amount becomes excess.

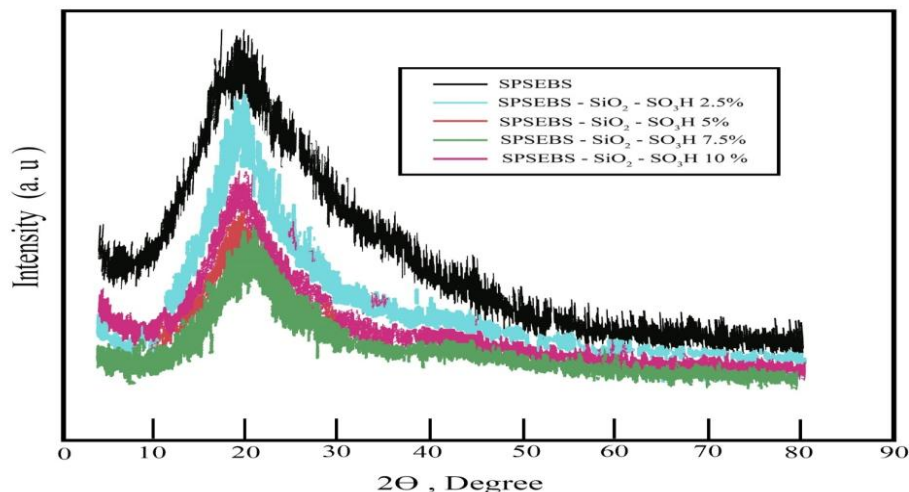


Fig. 3 XRD analysis of composite membranes

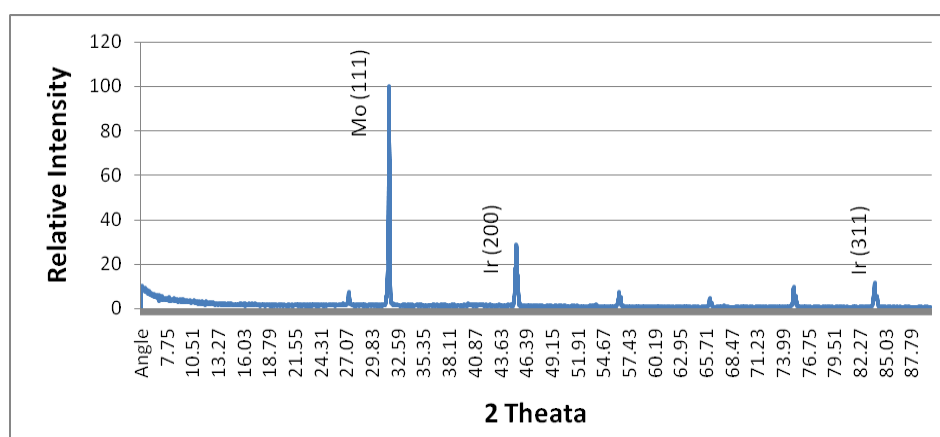


Fig.4 XRD analysis of Ir-V-Mo/C

Fig.4 shows the XRD analysis of Ir-V-Mo/C catalyst. It is clear that Ir and Mo are present. From the XRD analysis, the particle size was found out to be around $\sim 30\text{nm}$.

FTIR

In the spectrum of pure SiO_2 powders (fig 5), the peak seen at 1100 cm^{-1} corresponds to Si-O-Si bonds vibration for the pure amorphous silicon dioxide. The peak at 960 cm^{-1} is due to Si-OH stretching vibration. In case of SiO_2 - SO_3H (fig 6), a peak is seen at 1171 cm^{-1} attributing to Si-O- SO_3H stretching vibration. This peak confirms the sulfonation. The intensity of peak at 1100 cm^{-1} is observed to be decreased than that of the unsulfonated SiO_2 and similarly at the peak 960 cm^{-1} also.

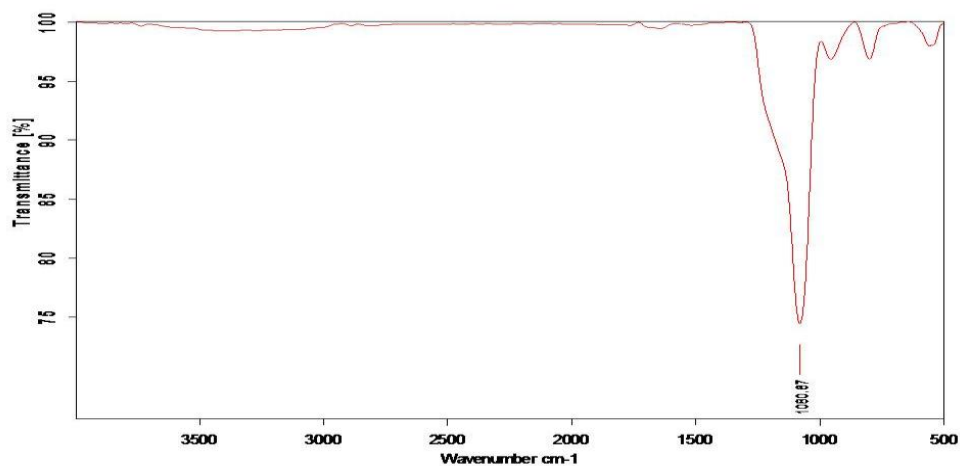


Fig.5 FTIR analysis of SiO₂

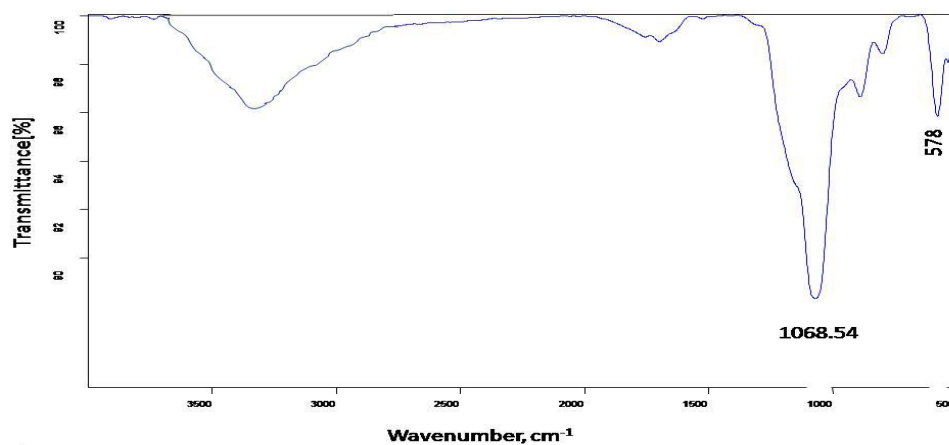


Fig.6 FTIR analysis of sulfonated SiO₂

Fig.7 shows the FTIR spectra of composite membranes. The unsulfonated membrane shows the highest peak intensity at 1020 cm⁻¹. In case of other membranes this peak intensity gets decreased. This can be attributed to the increment in hygroscopic property with the addition of sulfonated SiO₂.

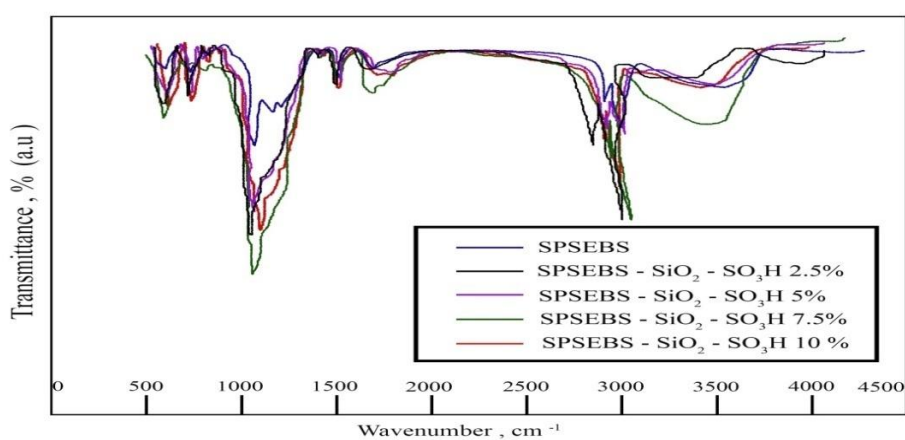


Fig.7 FTIR spectra of composite membranes

Fig.8 represents the FTIR spectrum of graphite oxide. For graphite oxide, aromatic content appears at 618.25 cm⁻¹, epoxy groups at 1113.89 cm⁻¹, C=C stretching at 1434.01 cm⁻¹, C=O and C-O stretching at 1582.02 cm⁻¹. The peak at 3417.12 cm⁻¹ is due to the stretching of -OH bonds.

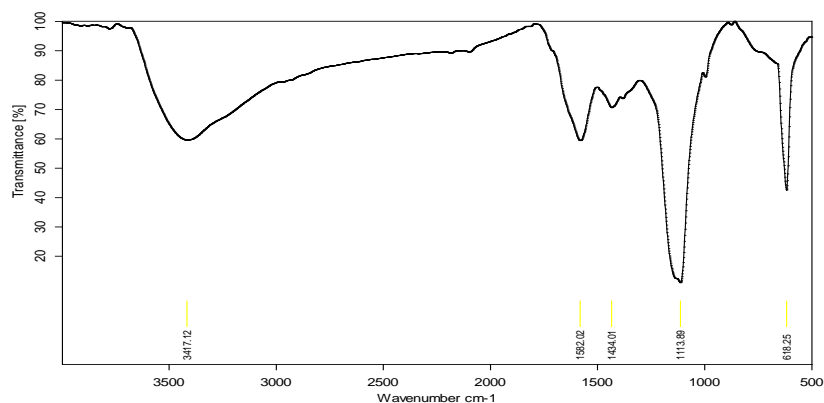


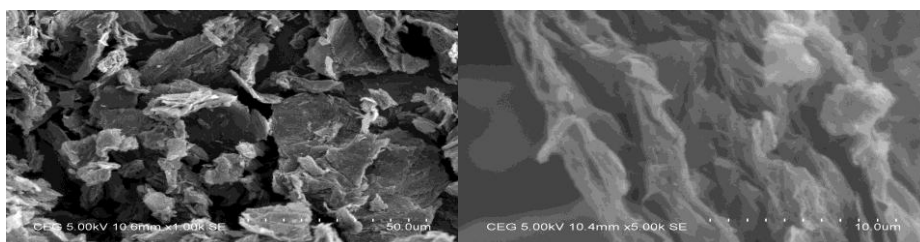
Fig.8 FTIR Spectrum of Graphite Oxide.

SEM

Fig.9 shows the SEM images of the SPSEBS-SiO₂-SO₃H 7.5% composite membrane. The image shows the homogeneous distribution of sulfonated silica throughout the SPSEBS polymer matrix.

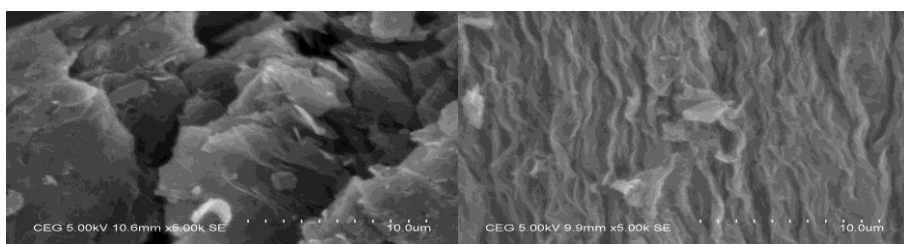


Fig.9 SEM image of SPSEBS-SiO₂-SO₃H 7.5% composite membrane



(a)

(b)



(c)

(d)

Fig.10 (a),(b),(c) are SEM images of Graphite Oxide at different magnification and orientation. (d) is the SEM image of reduced Graphene Oxide.

Fig.10 (a),(b),(c) shows images of graphite oxide. The random orientation and wavy appearance of exfoliated graphite oxide is seen from the SEM images. In Fig.10 (d), the formed graphene sheets showed wrinkled appearance, which are very thin.

3.6 ICP-OES

$$\text{Wt\%} = \frac{\text{Concentration in PPM (Instrument value)} * \text{Volume in ml} * \text{Dilution factor} * 10^{-4}}{\text{Weight of sample in g}}$$

Table2. ICP-OES of Ir-V-Mo/C

Sample ID	Elements Symbol Wavelength (nm)	Concentration
Sample 1 -----		
	Ir224.268	288.75 mg/L
	Mo 202.030	71.25 mg/L
	V 309.311	73.50 mg/L

From the above analysis, the composition of the elements iridium, vanadium and molybdenum present in the synthesized catalyst was found as 38.5%, 9.5% and 9.8% with respect to carbon support.

Proton Conductivity

The proton conductivity is one of the crucial parameter in the PEMFC applications. The increment in proton conductivity of the composite membranes was associated with the increase in acidic sites due to sulfonated SiO₂. It was very clear from Fig.11 that, the optimum percentage of addition of sulfonated silica into the SPSEBS matrix was 7.5%.

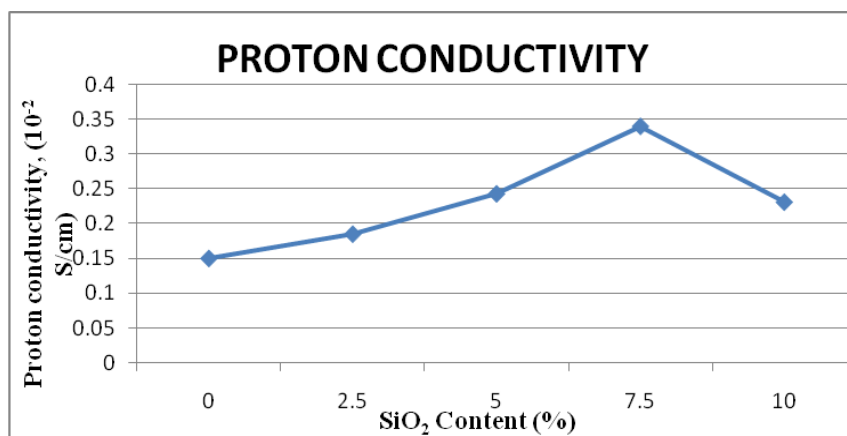


Fig.11 Proton conductivity of composite membranes.

Conclusion

The synthesized anode catalyst, Ir-V-Mo/C showed potential replacement for Pt/C commercial catalyst as evident from the CV analysis. The sulfonation of PSEBS was successively carried out using chlorosulfonic acid. The composite membranes of SPSEBS blended with the filler material, sulfonated SiO₂ were prepared by solution casting technique. The sulfonated metal oxides, sulfonated polymer and their composite membranes were characterized by XRD, SEM and FTIR techniques. Ion exchange capacity, water uptake and proton conductivity were measured for the composite membranes. The sulfonation of metal oxide induced an increase in the number of sulfonic acid groups, which significantly increased the proton conductivity of the sulfonated composite membranes. These sulfonated composite membranes are expected to show higher performance than the non-sulfonated composite membranes. This was due to the addition of sulfonated SiO₂ particles, whose higher proton conductivity and good water absorbing properties facilitated an effective proton transfer in the composite membranes. Among the prepared composite membranes, SPSEBS-SiO₂-SO₃H 7.5% showed the best proton conductivity.

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