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**POLYMER ELECTROLYTE MEMBRANE FROM CLOISITE 30B BASED SOLID PROTON
CONDUCTOR AND SULFONATED POLYETHER ETHER KETONE / POLYVINYLIDENE
FLUORIDE-CO-HEXAFLUORO PROPYLENE BLENDS FOR DIRECT METHANOL FUEL CELL**

Prasad M¹, Smita Mohanty^{1,2}, Sanjay K Nayak*^{1,2}

¹Central Institute of Plastics Engineering & Technology (CIPET), Chennai, India

²Laboratory for Advanced Research in Polymeric Materials (LARPM), Bhubaneswar

Prof (Dr.) S. K. Nayak

Professor & Chair

Laboratory for Advanced Research in Polymeric Materials (LARPM)

Central Institute of Plastics Engineering and Technology,

Bhubaneswar-751024

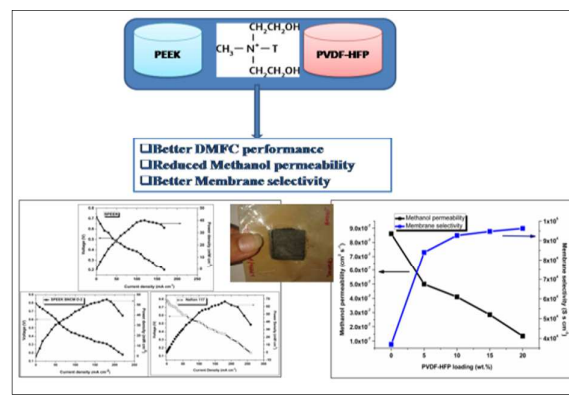
Odisha, India.

Email: papers.journal@gmail.com

Phone No: 0674 2742852

Fax No: 0674 2740463

Running head: Blend nanocomposite polymer electrolyte membranes for DMFC applications



- The improved Fuel Cell Performance of Polymer Electrolyte Membranes from C 30B filled sulfonated Polyether Ether Ketone / Polyvinylidene Fluoride-co-Hexafluoro Propylene blend indicates its candidature for DMFC Application

POLYMER ELECTROLYTE MEMBRANE FROM CLOISITE 30B BASED SOLID PROTON CONDUCTOR AND SULFONATED POLYETHER ETHER KETONE / POLYVINYLIDENE FLUORIDE-CO-HEXAFLUORO PROPYLENE BLENDS FOR DIRECT METHANOL FUEL CELL

Abstract

Polymer electrolyte membrane (PEM) was developed for direct methanol fuel cell (DMFC) based on sulfonated polyether ether ketone (SPEEK) and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) filled with Cloisite 30B (C 30B) as solid hydrophilic proton conductor. PEMs were characterized using liquid uptake, oxidative stability, TGA, XRD, SEM, AFM and impedance analysis. The single cell DMFC performance reveals that PEM showed an open circuit voltage (OCV) of 0.79 V and maximum power density value of 55 mWcm⁻² with a proton conductivity value in the range of 10⁻² S/cm. The methanol permeability and selectivity ratio of optimized membrane was 1.35 x 10⁻⁷ cm² s⁻¹ and 9.63 x 10⁴ S s cm⁻³ respectively. As a result fabricated membranes could be seen as promising PEM for DMFC applications.

Keywords: Blend nanocomposite membranes; Sulfonation; PEM; C 30B; PVDF-HFP

1. INTRODUCTION

Among the various types of fuel cells, direct methanol fuel cells (DMFCs) becomes the best choice because of its easy handling and its high energy density at very low operating temperatures.¹ Polymer electrolyte membranes (PEMs), a major component used in DMFC is still Nafion® based perfluorinated membranes. Nafion® membrane shows high proton conductivity at room temperature, as well as good mechanical and chemical stability. However, the decreased proton conductivity at low humidity, high cost and high methanol fuel permeability are the main technical hitches for using them in DMFCs.²⁻⁵

Sulfonated polyether ether ketone (SPEEK) is a promising alternative PEMs, as they acquire good thermal and oxidative stability, film forming property and high proton conductivity. Conversely, the disadvantages like higher swelling degree at high sulfonation degree, which lead to dimensional unsteadiness, methanol fuel permeability from anode to cathode during the operation of DMFCs and lower oxidative stability. Additionally, SPEEK membranes are known to have poor compatibility with the electrode containing Nafion binder and results in difficulties during the membrane electrode assembly (MEA) preparation.⁶ Hence filled counterparts of these sulfonated polymers such as nanocomposites or blend nanocomposites of SPEEK have been reported to be used for a wide array of fuel cell applications under variable conditions to achieve improved DMFC performances.⁷⁻¹⁶

The addition of hygroscopic solid inorganic proton conductors like nanoclays to the polymeric matrix enhances its ability to maintain sufficient humidity inside the membranes, and thus it improves proton conductivity.¹²⁻¹⁶ Moreover, by the choice of a suitable hydrophilic nanoclays, the possibility of a decrease in methanol permeability by means of tortuous pathways occurred; and which improves the performances of PEMs in DMFC.^{11,15} In this regard, it seems possible to improve the performance of PEMs by choosing suitable nanofiller.

Further to improve the dimensional stability and compatibility of SPEEK membranes to the Nafion electrode binder solution, a very cost effective blending technique with a hydrophobic polymer makes better control in swelling degree and dimensional stability without much loss of the proton conductivity values.¹⁷⁻²⁴ Song et.al¹⁷ prepared a cost-effective blend nanocomposite membrane of SPEEK with PVDF polymer and discusses

the effect of PVDF content on water uptake, swelling ratio, proton conductivity. Also, Jung et.al¹⁸ have developed a blend membrane with partially sulfonated polystyrene (SPS) and partially sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO) which exhibits relatively higher proton conductivity and methanol permeability than those of single component, SPS and SPPO respectively. Unveren et al²² fabricated a SPEEK/ PVDF blend and have observed from their study that the properties of fuel cell blend membranes depend not only on finding the suitable polymer combinations but also on the molecular weights of the polymers.

In this current study, prepared a blend nanocomposite PEMs in which hydrophilic C 30B nanoclays are dispersed in SPEEK/polyvinylidene fluoride-co-hexafluoro propylene (PVDF-HFP) blend system. We studied the capability of prepared PEMs for DMFC applications by evaluating their liquid uptake, proton conductivity, oxidative stability, thermal stability. The electrochemical performance of superior membrane was investigated in the DMFC setup.

2. Experimental Section

2.1 Materials

Victrix PEEK (grade 450G), was supplied from Victrix PLC (England), used as the base polymer. Kynar flex 2801, PVDF-HFP (11-12% of hexafluoropropylene copolymer) was supplied by Arkema, India. Organically modified nanoclay, C 30B with a cation exchange capacity (CEC) of 90 meq/100 g was procured from M/s Southern clay Products. Conc.H₂SO₄ (98% pure) used as sulfonating agent was supplied by Merck lab grade. The catalysts, Pt black for the cathode and Pt/Ru black for the anode, were purchased from Johnson-Matthey, USA. Nafion® 5 wt-% binder solution from E.I. DuPont Company was used for MEA preparation. Nafion 117 membrane, from E.I. DuPont Company was chosen as the commercial sample to compare the obtained results.

2.2 Sulfonation of PEEK

The sulfonation of PEEK was carried out using conc. conc.H₂SO₄ according to the procedure described elsewhere.^{12,16} In brief; 10 g of predried PEEK polymer was gradually added into vigorously stirred 350 ml of conc.H₂SO₄ at room temperature. After desired reaction time of 70 h, the sulfonated PEEK (SPEEK) was recovered by precipitating

it in excess ice cold water. Then the precipitate was repeatedly washed with deionised water until it reaches at p^H 6–7. After neutralizing, the SPEEK precipitate was kept in a vacuum oven at 100°C until it is completely dried. The obtained SPEEK with a DS = 67% was used for further experiments. The degree of sulfonation (DS) has been determined via volumetric titration using standard sodium hydroxide (NaOH) solution with phenolphthalein as an indicator by using the Equation (1).²⁵ In this study, SPEEK with DS = 67 % was used as a base matrix for membrane preparation.

$$DS (\%) = \left(\frac{0.291M(\text{NaOH}) \times V(\text{NaOH})}{W - 0.08M(\text{NaOH}) \times V(\text{NaOH})} \right) \times 100 \dots \dots \dots (1)$$

Where,

M (NaOH) is the concentration of standard NaOH solution (mol/l),

V (NaOH) is the volume of the NaOH solution used to neutralise (ml),

W is the sample mass (g),

291 is the molecular weight of PEEK monomer unit,

81 is the molecular weight of the $-\text{SO}_3\text{H}$.

2.3 Preparation of blend nanocomposite membranes

The SPEEK blend nanocomposite membranes were prepared by solution casting method according to scheduled formulation (Table 1). Dried SPEEK polymer was dissolved in DMAc for 6 h; a further 5 wt-% of C30B was added to the SPEEK solution and stirred for 3 h in an ultrasonic bath. Subsequently, different wt-% of PVDF-HFP powder is added to SPEEK/C30B solution and stirred for about 6 h followed by ultrasonication for 2 h. The resulting solution was casted on a glass plate and dried under vacuum at 80°C for 12 h and peeled off from the glass plate.

2.4 DMFC single cell performance test

All the membranes were pre-treated with dilute sulfuric acid solution for 24 h. MEA was prepared by hot pressing the anode and the cathode catalyst layer onto optimized PEM composition. The active surface area of the MEA was 5 cm^2 and was composed of Pt: Ru alloy supported carbon catalyst used for anode and Pt-black was used as catalyst for the cathode respectively. The addition of Nafion binder solution during the catalyst preparation bridges the active sites of catalysts as well as between catalysts and membranes in the interface. Then the slurry of catalyst was brushed directly (4 mgcm^{-2}) onto the membranes,

and hot pressed at 120 kgcm^{-2} pressure and 100°C . A fuel cell test station Won A Tech, Korea was used for evaluating the performance by measuring the cell voltage versus current density at 70°C . Air with a flow rate of 500 cc min^{-1} and methanol (2M) with a flow rate of 10 cc min^{-1} was supplied to cathode and anode respectively. Once the temperature reached at 70°C , the DMFC performance measurement was conducted three times, and the results were represented as the average data.

2.5 Membrane characterization

2.5.1 Liquid uptake of the membranes in water/ methanol solution and swelling degree

The membranes were dried in a vacuum oven at 60°C for 24 h and were cut into $2 \text{ cm} \times 2 \text{ cm}$ to determine its dry weight (W_d), length (L_d) and area (A_d), respectively. The membranes were immersed in deionised water at a predetermined temperature for 24 h and then at elevated temperature i.e. 70°C for 2 h for water and methanol uptake analysis. The water uptake/methanol uptake of all the membranes was determined from the difference in weight between the dry and swollen membranes in water/methanol using the following Equation. (2)

$$\text{Water/methanol uptake (\%)} = \frac{(W_w - W_d) \times 100}{W_d} \dots\dots\dots (2)$$

Similarly, the swelling ratio of membranes was measured by immersing the various dried membrane in aqueous solutions at a predetermined temperature for 24 h and then at elevated temperature i.e. 70°C for 2 h, respectively. After desired time, the length (L_w) and area (A_w) of the membranes were determined by wiping off the surface water with a piece of filter paper. The swelling ratio was calculated by using the Equation. (3) and (4)

$$\text{Swelling degree of length (SD}_L, \%) = \frac{(L_w - L_d) \times 100}{L_d} \dots\dots\dots (3)$$

$$\text{Swelling degree of area (SD}_A, \%) = \frac{(A_w - A_d) \times 100}{A_d} \dots\dots\dots (4)$$

2.5.2 Oxidative stability by Fenton's reagent test

Oxidative stability of the membranes was tested by immersing the membrane sample into 50 ml of Fenton's reagent (30% H_2O_2 containing 30 ppm FeSO_4) at room temperature for 5 h. After desired time, the samples were taken out of the solution and

weighed again. Oxidative stability was evaluated from the percentage of weight loss of the membrane sample.

2.5.3 Thermogravimetric Analysis (TGA)

Thermal stability of the membranes was determined using a thermogravimetric analyzer (Q 50, M/s TA Instruments). The membranes were heated from room temperature to 800°C at a heating rate of 20°C/min under nitrogen atmosphere.

2.5.4 Wide angle X-Ray Diffraction (WXR)

The dispersion of C 30B particles in the hybrid membranes was successfully determined by WXR studies. The test was performed by a X-Ray diffractometer (M/s Shimadzu, Kyoto, Japan) using a Cu K α ray of wavelength 1.54 Å over the range $2^\circ \leq 2\theta \leq 25^\circ$ at 40kV.

2.5.5 Membrane morphological studies

Surface and cross sectional morphology of the membranes were investigated by using scanning electron microscopy (SEM) EVO MA 15 (M/s Carl Zeiss SMT Ltd, Germany) equipment at 10 kV. The samples were sputter coated with gold/palladium prior to imaging.

The phase morphology of membranes was studied using atomic force microscopy (M/s Park Autoprob, Korea) in non-contact mode.

2.5.6 Proton conductivity measurements

Proton conductivity of fully hydrated membranes was measured by the AC impedance spectroscopy technique over a frequency range of 1-10⁶ Hz with oscillating voltage 10 mV using a impedance spectroscopy (ZIVE-SP2, M/s Won A Tech Co. Ltd., Korea) at room temperature and 70 °C. Circular sample of 10 mm diameter was cut from the membrane and are clamped between two blocks of stainless steel electrodes. The proton conductivity (σ) was calculated from the following Equation. (5).

$$\sigma \text{ (S/cm)} = d/RS \dots \dots \dots (5)$$

Where, d and S are the thickness of the samples in cm and the face area of the membranes in cm^2 , and R is the resistance offered by the membranes in ohms.

2.5.7 Methanol permeability measurements

Methanol permeability measurements of various membranes were conducted by using a glass diffusion cell. Compartment A was filled with 50 ml of 2M methanol solution while compartment B was with the same amount of deionised water. Prior to the test, all the membranes were pre-hydrated for at least 24 h. The membrane with an active surface area of 4.91 cm^2 was clamped tightly between two glass compartments. The concentration of methanol solution diffused from compartment A to B across the membrane was continuously examined with time using a digital density meter (DMA 5000, M/s Anton Paar) at a time interval of every 30 m. Before the experiment, the calibration curve for the density vs. the methanol concentration was prepared to measure actual methanol concentration in the compartment B. From the straight line plot of methanol concentration vs. permeation time, methanol concentration C_B can be calculated by using the given Equation. (6).

$$C_B(t) = \frac{A P C_A (t-t_0)}{(V_B) L} \dots\dots\dots (6)$$

where C_A and C_B are the concentration of methanol in compartment A and B (in mol L^{-1}); A (in cm^2) and L (in cm) are the effective area and thickness of the membranes; P is the methanol permeability (in $\text{cm}^2 \text{ s}^{-1}$); V_B is the diffusion compartment volume (in cm^3); $(t-t_0)$ is time a lag (in seconds).

3. Results and discussion

3.1 Liquid uptake and swelling ratio of membranes

The amount of water content has a major effect on the proton conductivity of the PEMs. Generally the proton transport through membranes requires a well-connected channel formed by ionic clusters of hydrophilic sulfonated functional groups. But too much water absorption of the membranes results in unstable membrane. The higher water uptake value of the membranes will enhance its swelling ratio leads to decrease in mechanical stability of membranes.

Fig.1**Table. 1**

It was observed from Fig.1 and Table.1 that, the SPEEK blend nanocomposite membranes with 5 wt-% of C 30B exhibited a decreasing tendency in water, methanol uptake and swelling degree (both SD_L and SD_A) values with the incorporation of PVDF-HFP. At 25°C, with the introduction of 25 wt-% of PVDF-HFP, the water uptake values decreased from 25.10% to 11.36% and methanol uptake values decreased from 24.72% to 14.21%. Similarly, the blend nanocomposite PEM with 25 wt-% of PVDF-HFP showed an SD_L and SD_A value of about 12.32% and 8.31% respectively, which is a most favourable swelling degree values with an excellent dimensional stability. Also at higher temperature, all the blend nanocomposite membranes showed a comparatively low liquid uptake and swelling degree values with the addition of PVDF-HFP. It is expected that, the lower swelling degree values of SPEEK blend nanocomposite membranes will improve the dimensional stability and maintain the contact between PEM and the catalysts, which can improve the DMFC performances.

The decrease in liquid uptake and swelling degree values can be explained as follows. The introduction of hydrophobic PVDF-HFP causes a larger average separation between the two neighbouring $-SO_3H$ groups, which caused to decrease the formation of hydrophilic ionic clusters and water/ methanol uptake values.^{19,20} Conversely, the addition of C 30B nanoclay facilitates to form an inter-molecular hydrogen bonding with $-SO_3H$ group of SPEEK and water as well as methanol molecules, and retain membrane hydrophilicity.^{11,12, 26} Hence, the addition of C 30B nanoclay maintains the membrane liquid uptake characteristics and the hydrophobic PVDF-HFP polymer controlling its dimensional stability. Also, it has been evident that the liquid uptake and swelling degree values of the SPEEK blend nanocomposite membranes were lower than the standard Nafion 117 membrane.

3.2 Oxidative stability

The chemical/oxidative stability of PEM under fuel cell operating conditions is a vital issue affecting directly on the operation and durability of DMFCs. Peroxide radicals are responsible for chemical attack on the membrane material. In this work, the oxidative stability of the membranes was investigated in a 30% H_2O_2 aqueous solution at room

temperature. From the Table 1, it was noticed that the addition of 5 wt-% of C 30B and 25 wt-% of PVDF-HFP to SPEEK system increases its weight residue from 92.10% to 99.30% after the Fenton's test. The weight loss of pure SPEEK membrane in 5h at room temperature was 7.9 wt-%, while for Nafion 117 was found to be 2.2 wt-%. As shown in the Table 1, blend nanocomposite membrane is considered to be more stable against peroxide radicals than pure SPEEK membrane. Hydrophobicity and chemical stability of PVDF-HFP improves its resistance to attack towards free radical formation during the fuel cell operation reaction. This enhanced stability may be due to the restriction of movement of highly active free radicals within the blend nanocomposite membrane system for the attack towards the PEM.^{7, 11, 22}

3.3 Proton Conductivity

The proton conductivity value at 25°C and 70°C of all membranes were measured and represented in Table 1. Prior to measurements, all membranes were fully hydrated in deionised water for 24 h at room temperature. The proton transport in membranes requires a well interconnected channels formed by ion clusters of hydrophilic sulfonated ionic cluster functional groups. The diameter of interconnected channels has significant effects on the proton conduction rate in membranes. It has been observed from Table 1 that the proton conductivity values of Nafion 117 and SPEEK at 25°C were 7.10 and $3.18 \times 10^{-2} \text{ S cm}^{-1}$ respectively. Also it is evident that at 25°C and 70°C, with the addition of 20 wt-% of PVDF-HFP, a percentage reduction of 72.87% and 74.88% was observed in proton conductivity values. The introduction of hydrophobic PVDF-HFP reduces the density of hydrophilic sulfonic acid groups on the SPEEK and content of interconnected ionic channels perhaps decreased; thus reduces the proton conductivity values. At the same time, the addition of hydrophilic C 30B in SPEEK/PVDF-HFP blend system forms a conducting ionic channel, which helps to retain water molecules within the membrane structure at higher temperature, thus it maintain the proton conductivity.^{27, 28} Proton conductivity of the Nafion 117 was also measured under the same experimental conditions for comparison purpose. Further, the membranes with 25 wt% of PVDF-HFP, i.e. SPEEK BNCM E-2 blend nanocomposite PEMs showed a lower proton conductivity values in the order of $10^{-3} \text{ S cm}^{-1}$.

The determination of optimum loading of PVDF-HFP has been done by comparing the liquid uptake values, swelling degree, oxidative stability of all blend nanocomposite membranes. Also, apart from dimensional unsteadiness and heterogeneous

surface observed in case of SPEEK BNCM E-2, beyond 20 wt% of PVDF-HFP loading there was a considerable decrease in the values of proton conductivity. Since, the primary objective of our study is to improve the dimensional and oxidative stability, lower swelling degree and methanol permeability without much drop in proton conductivity values, blend nanocomposite membrane having a composition with 20 wt% of PVDF-HFP was optimized and used for the further characterisation studies related to DMFC applications.

3.4 Wide angle X-ray diffraction (WXR)

Generally the nanostructure of blend and nanocomposites is typically characterized using XRD techniques. Fig.2 illustrates XRD patterns of the PVDF-HFP, SPEEK and SPEEK BNCM D-2 blend nanocomposite membranes. As seen in Figure 2, two sharp diffraction peaks appeared at 2 theta corresponds to 18.4° and 20.18° correspond to the (1 0 0) and (0 2 0) reflections of semi-crystalline structure of PVDF-HFP.^{24, 29} Due to the introduction of sulfonic acid groups in the structure, SPEEK membrane shows amorphous characteristics by showing a wide diffraction peak. From the diffraction patterns, it was found that the sharp crystalline diffraction peaks of PVDF-HFP broadened in the presence of SPEEK and C 30B nanoclay. This may propose that the addition of SPEEK induced significant disorder into the PVDF-HFP polymer. When C 30B was introduced to the SPEEK/PVDF-HFP blend system, there is no sharp deflection within the scattered angle limit, suggests the possibility for extensive exfoliation of polymeric molecules within C30B layers.¹⁷

Fig.2

3.5 Thermal stability: TGA study

Thermal stability of the prepared SPEEK and SPEEK BNCM D-2 membranes were studied by TGA and the results are represented in the Fig.3. Both membranes showed multiple step degradation; in which first step degradation below 200°C is mainly attributed to the loss of moisture or residual solvents. In continuation, the major weight loss occurred in SPEEK and SPEEK BNCM D-2 between $\sim 200^\circ\text{C}$ - 400°C is mainly associated with the desulfonation process of the sulfonic acid group in SPEEK matrix; which involves the evolution of SO_2 and SO gases.^{6,9,30} The transition observed in SPEEK membranes above 400°C is mainly due to the degradation of SPEEK polymeric main chain. The third weight loss beyond 400°C is mainly attributed to the degradation of polymeric chains of PVDF-HFP

initially and SPEEK chains secondly in the blend nanocomposite membrane system. Similar degradation characteristics have also been reported in the case of blend membranes of PVDF-HFP and SPEEK.^{19, 22} Also from the DTG thermogram, apart from the peak below 200°C which is associated with the evaporation of solvents and water molecules, separate peak has been observed corresponding to a desulfonation process (200-400°C) and degradation of polymeric chains of PVDF-HFP and SPEEK (above 400°C). Thus from TGA analysis, it is evident that SPEEK BNCM D-2 membrane shows sufficient thermal stability for the DMFC applications.

Fig. 3

3.6 Morphological Studies

SEM analysis of the membrane surface is an effective way to study the compatibility in polymer blend systems. The surface and cross-sectional morphology of SPEEK and its optimised blend nanocomposite membrane were studied by SEM. From Fig. 4 (a) & (c), a clear dense morphology can be observed for SPEEK membranes.¹¹ The cross-sectional morphology of membranes as seen in Figure 4 (d) revealed that miscibility behaviour between SPEEK and PVDF-HFP. SPEEK blend nanocomposite membranes showed a comparatively good adhesion between SPEEK and PVDF-HFP matrix. This might be due to the better interaction of C 30B nanoclay with polymeric blend matrix due to the polar-polar interaction. The improved homogeneous characteristics will help to retain water molecules within its ionic clusters; maintain its hydrophilicity and thus proton conductivity values. Also, the most favourable proton conductivity values observed for the SPEEK blend nanocomposite membranes might be correlated with its better homogeneity observed from SEM images.

Fig.4

To further validate the result of addition of hydrophobic PVDF-HFP on the microstructure of the membranes, non contact AFM images of SPEEK and SPEEK BNCM D-2 membranes were studied and their phase and three dimensional images have been represented in the Fig.5 (a-d). Generally in the AFM phase micrographs, dark regions are assigned to hydrophilic region and light regions are assigned to a hydrophobic region.^{31,32} Hence, the distribution and connectivity of the hydrophilic conductive channel have a great influence on the proton conductivity values of the membranes. The three dimensional AFM

images showed a combination of peaks and valley-like structures. It is known that a relatively uniform nodular structure on the membrane surface improves the hydrophilicity and thus favors the proton conduction. From Fig.5, SPEEK membrane showed a more continuous connectivity between hydrophilic channels which create a conductive pathway for the protons i.e. the presence of more continuous dark regions in the AFM phase micrographs. Also, three dimensional images revealed the fact that, SPEEK shows more continuous hydrophilic nodular channel as compared to SPEEK BNCM D-2. Thus the decrease in hydrophilic regions in the blend nanocomposite membranes i.e. SPEEK BNCM D-2 may direct impact on the reduction of liquid uptake, swelling degree, proton conductivity of the membranes.

Fig. 5

3.7 DMFC single cell performance test

Single cell DMFC performance curves for DMFC comprising Nafion 117; SPEEK and SPEEK BNCM D-2 at operating temperature of 70°C are represented in Fig.6. Generally, the open circuit voltage (OCV) is directly interrelated to the fuel cross over and generally, the higher the OCV, the lower the fuel crosses over.^{33,34} Moreover, higher OCV of membrane is due to the better compatibility between the catalyst layer and the membrane.³⁵ From our studied membranes, OCV obtained for SPEEK BNCM D-2 MEA is 0.79 V which is a similar value to Nafion 117 (showed a 0.78V). Thus, the polarization curve clearly proves that the incorporation of PVDF-HFP and C 30B in SPEEK matrix increases its DMFC performances by showing higher OCV values. Also from Fig.6, it has been observed that, the current densities for the SPEEK, SPEEK BNCM D-2 and Nafion 117 were measured as 23, 39 and 36 mA cm⁻² (at a potential of 0.4 V and 2M methanol concentration), respectively. The maximum power density of the SPEEK BNCM D-2 membrane was obtained as 55 mWcm⁻² compared to 64 mWcm⁻² for Nafion 117 at 2M methanol feed.

Interestingly, the SPEEK BNCM D-2 blend nanocomposite PEMs, even with a lower proton conductivity value than SPEEK has provided a higher DMFC output in terms of power density and OCV values, which is a very clear indication for the leading role of reduced methanol permeability with the incorporation of PVDF-HFP and C 30B. On the other hand, the other possible reason for the better DMFC performance of SPEEK BNCM D-2 may be due to the stable MEA interface; it showed a lower activation resistance value,

that improves the overall cell performances. Thus, lower methanol permeability and stable MEA interface improves the performances of the SPEEK BNCM D-2 blend nanocomposite membranes. Also the improvement in DMFC performance of SPEEK BNCM D-2 may be attributed to the lower swelling degree, better dimensional stability as well as oxidative stability.

Fig.6

3.8 Methanol permeability study

In addition to the proton conductivity and oxidative stability against the peroxide radicals, the methanol permeability value has a significant effect on the performance of PEM for DMFC applications. Methanol crossover through the PEM from anode to cathode is an undesirable situation because it leads to voltage drop during the performance of fuel cell. So methanol permeability should be also seen in the possible role of a new membrane material in DMFC. Membranes with lower methanol permeation are always preferable, and which gives maximum power density values and maximum open circuit voltage (OCV) value. Fig.7 shows the typical curve of methanol concentration vs. time for the investigated membranes using a 2M methanol solution. All values of methanol permeability tests for the PEMs were obtained from the slope of the straight line.

Fig.7

Also, Fig.8 and Table 1 describes the effect of addition of PVDF-HFP and C 30 B particles, i.e. reduction in methanol permeability values of SPEEK from $8.61 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ to $1.35 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ when PVDF-HFP contents increased to the tune of 5-20 wt-%. The decrease in methanol permeability of SPEEK BNCM D-2 blend nanocomposite membranes might be due the combined effect of hydrophobic PVDF-HFP and C 30B clay layers; which creates a longer diffusive torturous path way for methanol or some of the nanoscopic channels for passing methanol molecules are restricted.^{15, 29} For ideal DMFC applications, the PEM should have the lowest methanol permeability and highest proton conductivity values with maximum power density values. Hence the lesser methanol permeability and average proton conductivity values of SPEEK BNCM D-2 blend nanocomposite membrane is one of the significant advantages for using as PEM in DMFC system.

The term, membrane selectivity, defined as the ratio of proton conductivity to methanol permeability, is commonly used to evaluate the overall membrane performances. A membrane with higher selectivity is desired for DMFCs. As described in Fig.8, the selectivity of the membranes, increased with increasing PVDF-HFP contents. The membrane SPEEK BNCM D-2 had a higher selectivity in comparison with the SPEEK membrane, which was primarily due to the enhanced methanol barrier property. Among all the membranes investigated in this study, the blend nanocomposite membrane, SPEEK BNCM D-2 possessed the higher selectivity value than Nafion 117 membranes (shows only $8.74 \times 10^4 \text{ S s cm}^{-3}$) with lower thickness of membrane (100 μ). More importantly, the SPEEK/PVDF HFP/ C 30B blend nanocomposite PEMs is a cheap non-perfluorosulfonated polymer membrane, as compared to the standard Nafion membranes.

Fig.8

Conclusions

SPEEK/PVDF-HFP/C 30B blend nanocomposite membranes with improved dimensional, oxidative stability and optimum proton conductivity were prepared by solution casting method. The single cell DMFC performance reveals that SPEEK/PVDF-HFP/C 30B membranes showed OCV of 0.79 V and maximum power density value of 55 mWcm⁻² at 2M methanol feed, which confirmed the efficiency of PEMs suitable for DMFC application. In addition, the obtained methanol permeability of PEMs was lower than that of Nafion 117. Introduction of PVDF-HFP and C 30B collectively improved oxidative and dimensional stability of PEMs. The liquid uptake and the swelling ratio of membranes decreased with the increase of PVDF-HFP content; which led to improved MEA interface stability. TGA studies revealed sufficient thermal stability for DMFC applications. The improvements in the OCV value, oxidative, thermal and liquid uptake stability and higher selectivity ratio of the membranes could be achieved without much loss of proton conductivity values, makes it suitable PEMs for DMFC application.

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Table 1 Oxidative stability, proton conductivity, methanol permeability and selectivity ratios of various membranes

Membrane code	Mass ratio SPEEK/PVDF-HFP/C 30B	Oxidative stability test (wt-%)	Proton Conductivity $\times 10^{-2}$ (S/cm) ^a		Methanol permeability $\times 10^{-7}$ cm ² s ⁻¹	Selectivity $\times 10^4$ (S s cm ⁻³) ^b
			25°C	70°C		
SPEEK	100/0/0	92.1	3.18	4.98	8.61	4.15
SPEEK BNCM A-2	95/5/5	96.9	4.21	8.10	5.00	8.40
SPEEK BNCM B-2	90/10/5	97.8	3.81	6.32	4.10	9.27
SPEEK BNCM C-2	85/15/5	98.3	2.71	4.96	2.85	9.47
SPEEK BNCM D-2	80/20/5	99.1	1.31	2.14	1.35	9.63
SPEEK BNCM E-2	75/25/5	99.3	0.08	1.09
Nafion 117	97.8	7.1	8.4	8.12	8.74
^a These results are mean value of at least three trials for each sample.						
^b Proton conductivity to methanol permeability ratio.						

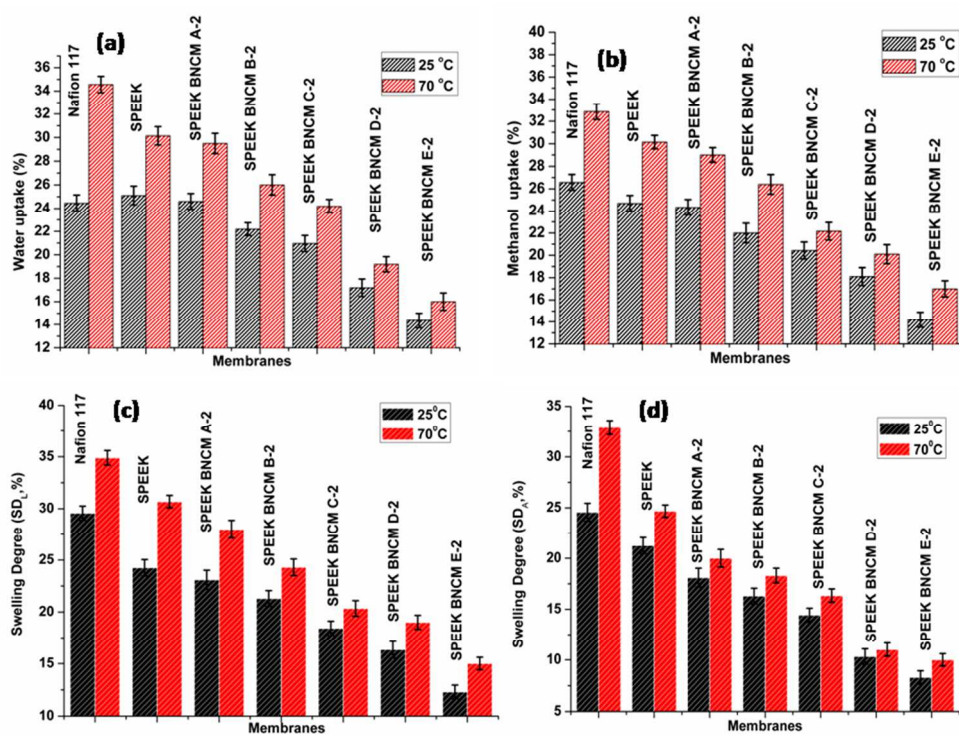


Fig. 1. Water uptake, methanol uptake and swelling degree values of the membranes 254x190mm (96 x 96 DPI)

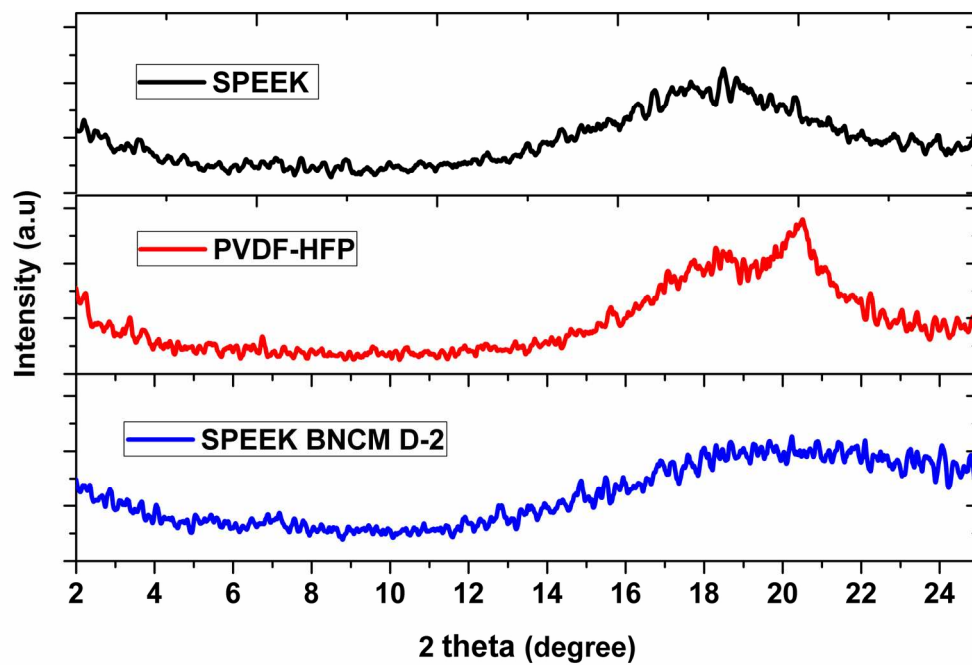


Fig.2. XRD plot of PVDF-HFP, SPEEK and SPEEK BNCM D-2 membranes
164x109mm (300 x 300 DPI)

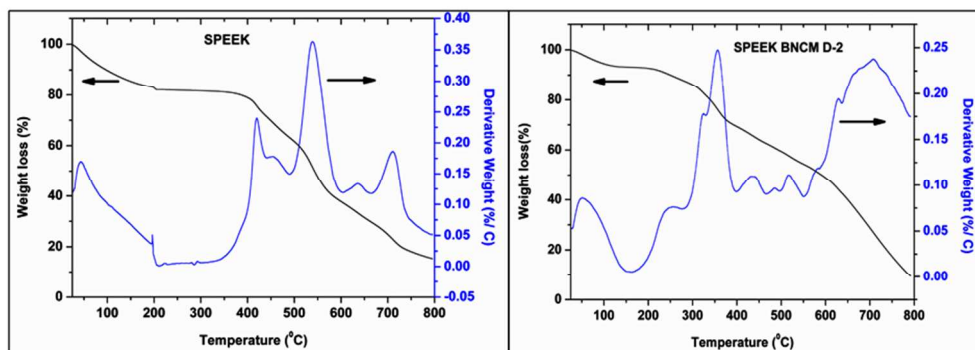


Fig. 3. TGA thermograms of SPEEK and SPEEK BNCCM D-2 membranes 254x95mm (96 x 96 DPI)

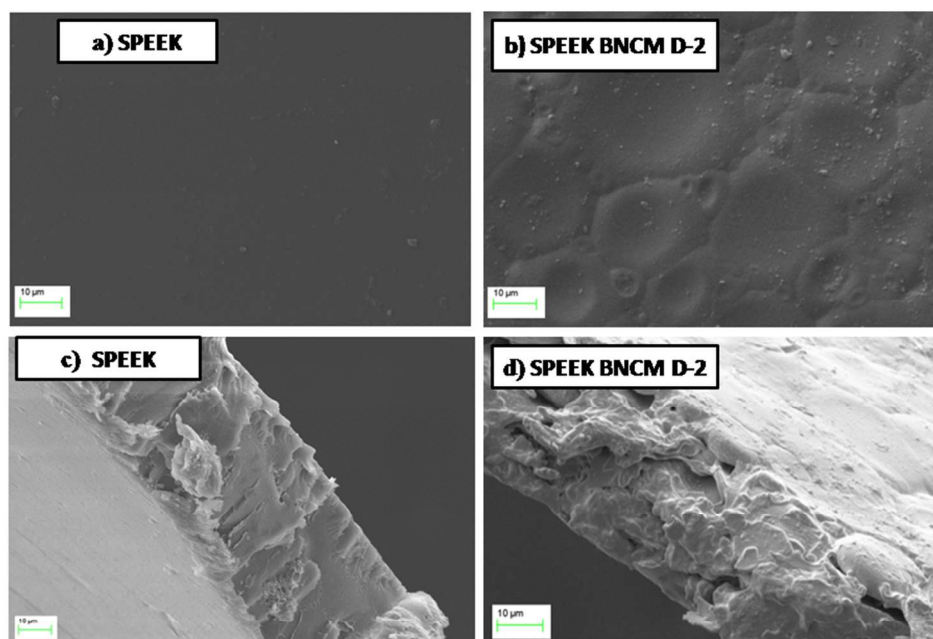


Fig.4. SEM images of (a) SPEEK surface, (b) SPEEK BNCM D-2 surface, (c) SPEEK cross section, (d) SPEEK BNCM D-2 cross section
254x190mm (96 x 96 DPI)

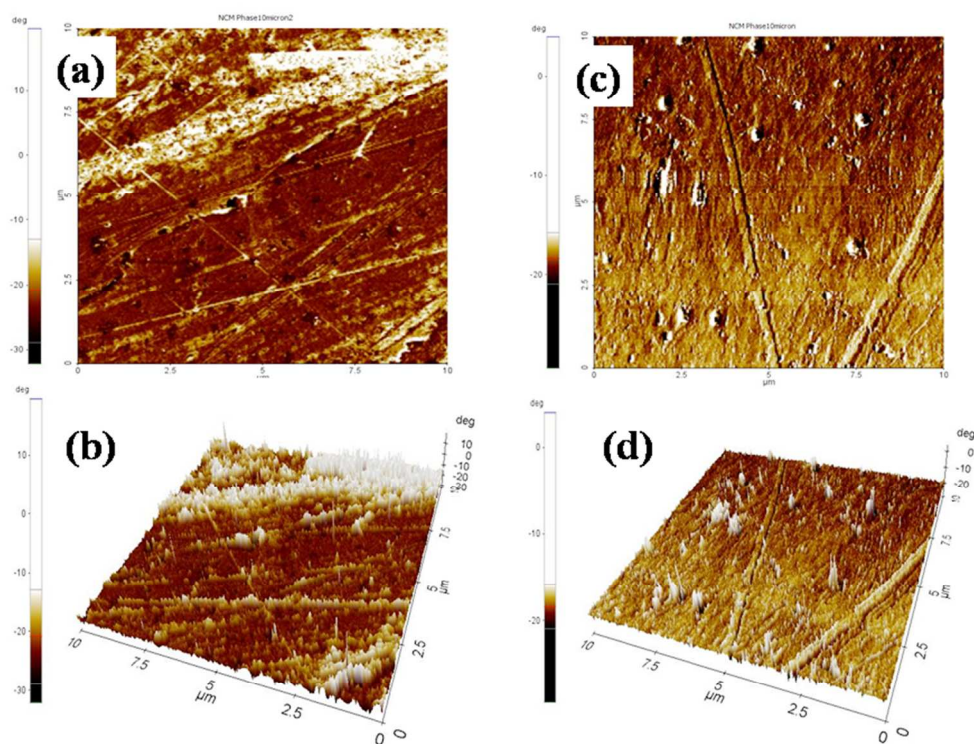


Fig. 5. AFM phase images (a) SPEEK and (c) SPEEK BNCD-2 membranes
Three dimensional images (b) SPEEK and (d) SPEEK BNCD-2 membranes

236x184mm (96 x 96 DPI)

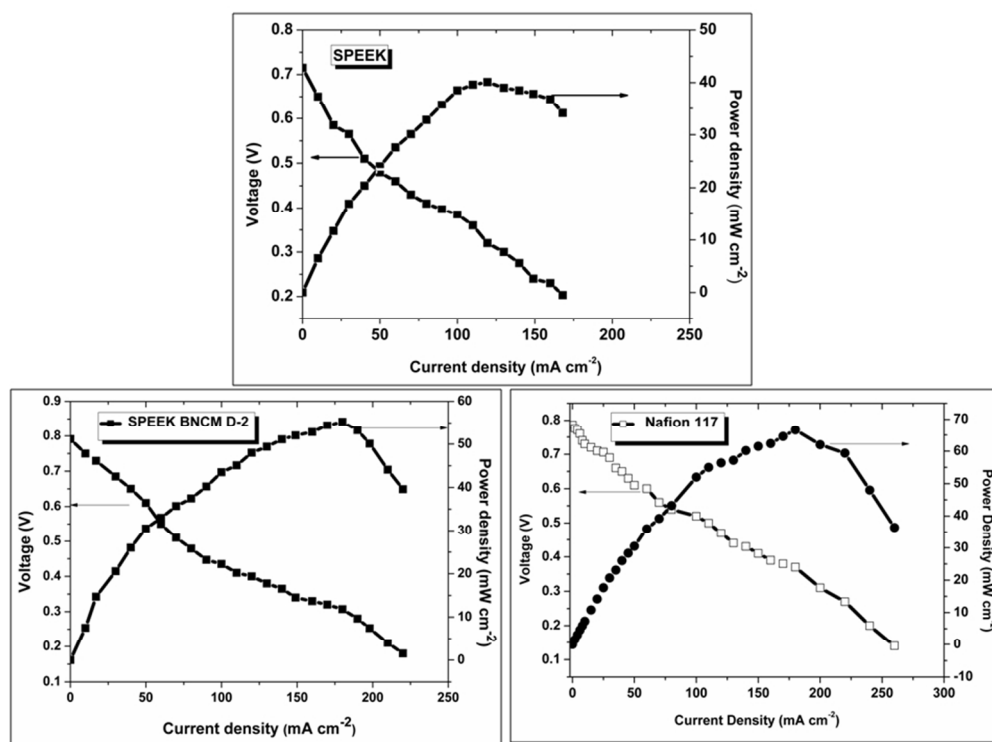


Fig.6. Polarization curves of SPEEK, SPEEK BNCM D-2 and Nafion 117 254x190mm (96 x 96 DPI)

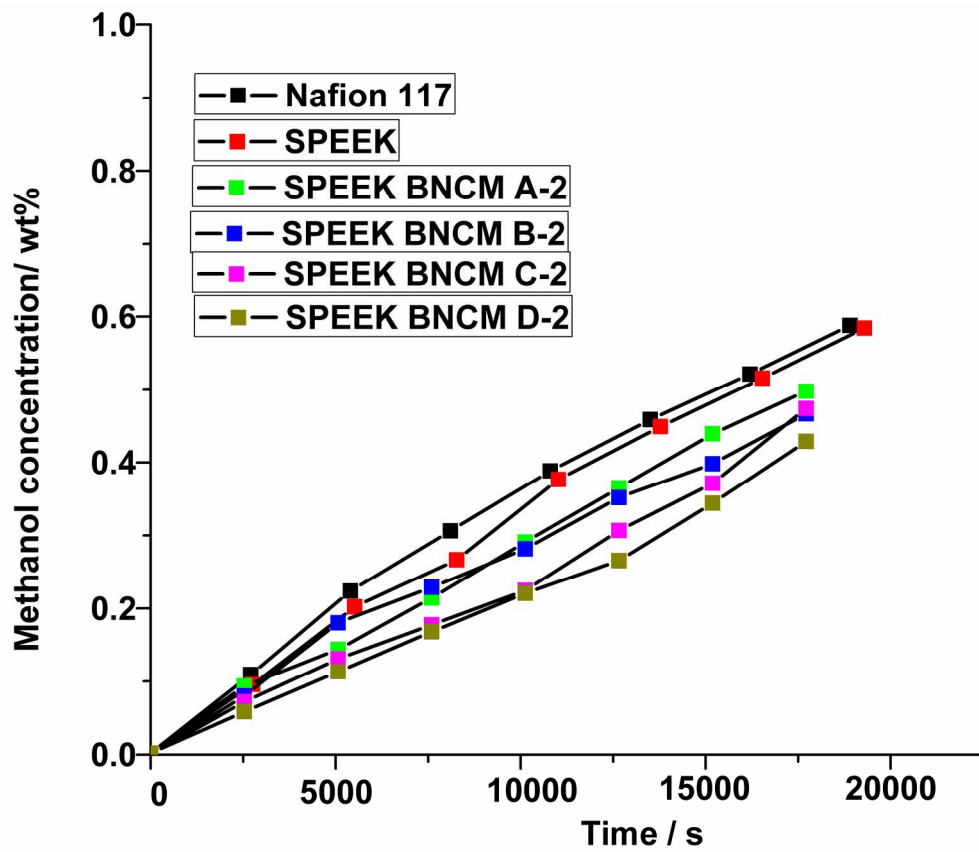


Fig.7. The methanol concentration vs. time curve for the membranes 201x174mm (300 x 300 DPI)

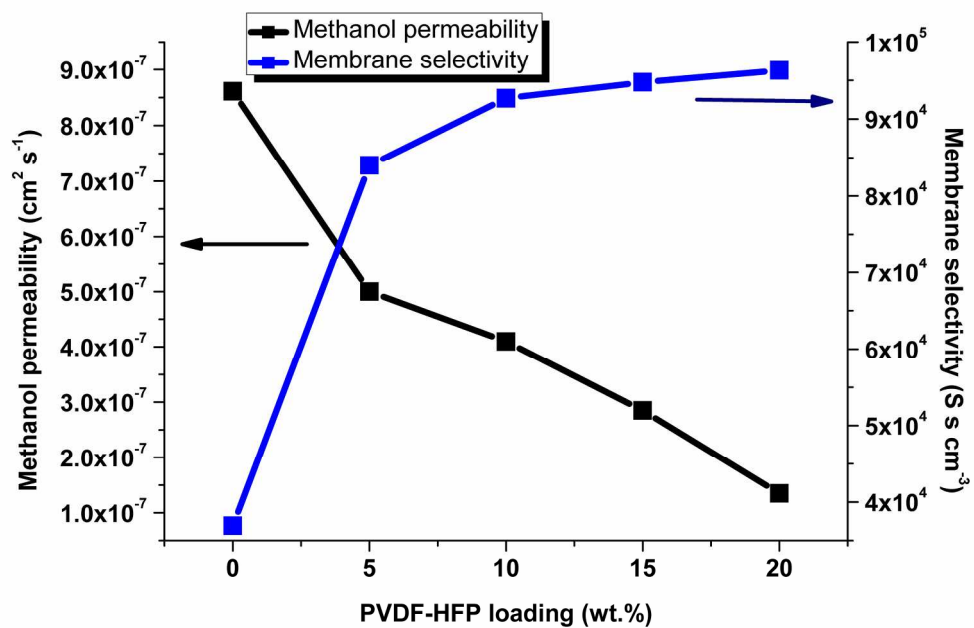
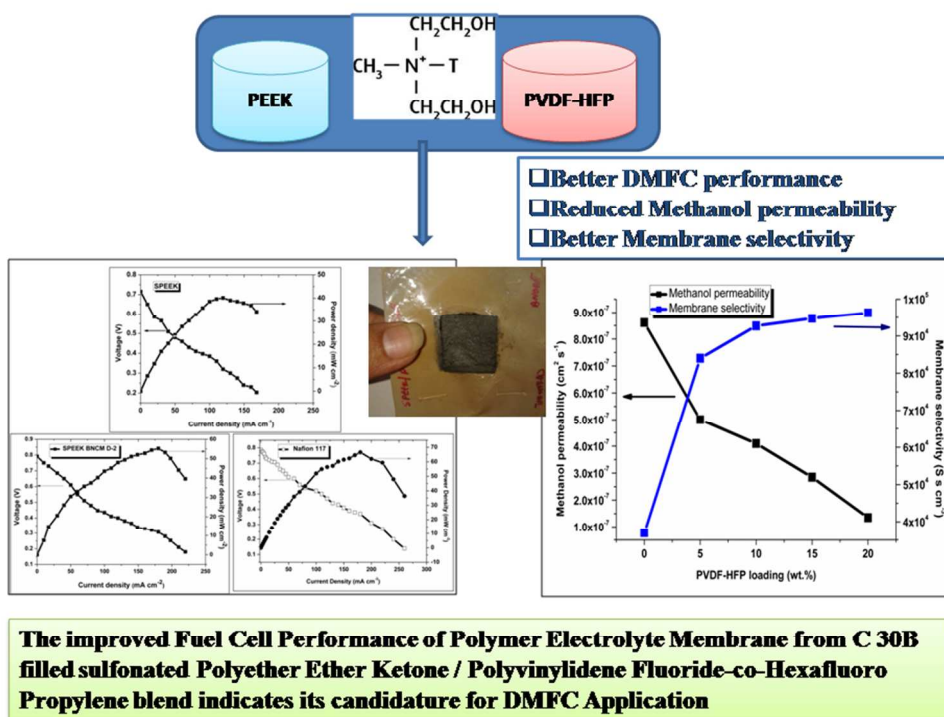


Fig.8. Methanol permeability and membrane selectivity values of fabricated blend nanocomposite membrane at various loading of PVDF-HFP containing 5 wt-% of C 30B 206x143mm (300 x 300 DPI)



Graphical Abstarct
254x190mm (96 x 96 DPI)