Sulphonated PEEK-Artocarpus Heterophyllus Based Composite Membranes for PEM Fuelcells

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Abstract- *Binary composite membrane of Sulphonated Poly Ether Ether Ketone (SPEEK) with Artocarpus heterophyllus (AH) as filler has been prepared by varying AH:SPEEK in five different ratios 0%:100% (SPEEK), 1%:99% (AH1), 2%:98% (AH2), 3%:97% (AH3), 4%96% (AH4): and 5%:95% (AH5) by solution casting technique at 80^oC environment. All the films are tested for their Ion Exchange Capacity (IEC), Chemical Stability (CS), Proton Conductivity (PC) and nonetheless Water Absorption (WA) performance. The observations on such parameters identified obviously the sample AH5 has accomplished the requisites for their suitability as an composite membrane for PEM fuel cells. To emphasis this authenticity than other Samples in terms of its complexation of binary constituents, FTIR; for explore it's crystalline/amorphous nature, XRD; sustanance of its thermal stability by TGA have been anchored on all five samples as prepared. FTIR vibrational studies confirm the sulphonation of PEEK, and degree of complexation of SPEEK with different concentration of AH. SEM surface profile of SPEEK and SPEEK/AH composite reveal that increase in AH in the composite detoriates the textenty of the membrane. XRD reveal that SPEEK is found to loose its crystalline characteristics and found in highly amorphous in AH5. Amorphosity paves the way for good flexible and durable membrane with requisite WA and protonic conductivity. The TGA thermal profile registers weight losses in three steps and there is no significant weight loss upto 230 $^{\circ}C$ suggests its suitability for operational conditions of PEMFC. The optimised AH5, as identified used for test fuel cell studies in real time PEMFC testing well augments its better performance with better OCV as well as good power density.*

Keywords- Polymer Electrolyte Membrane Fuelcell, SPEEK/AH composite, Proton conductivity, Water Absorption, Realtime PEMFC test

I. INTRODUCTION

As humanity advance, the energy need also goes up. To cater the need one has to exploit the nature. But usage of petroleum-based energy is not sustainable and also environment gets polluted beyond the tolerance limit. Polymer electrolyte membrane fuel cells (PEMFCs) have gathered attention and interest as alternative energy conversion devices for stationary and portable applications because of their high energy conversion efficiency and environmental friendliness [2-3]. The successful outcome of a PEMFC mainly depends upon the performance of proton exchange membrane (PEM), which is responsible for proton transfer from anode to cathode. To achieve higher efficiency, the membranes must possess good proton conductivity, low electron conductivity, least fuel cross – over, enough mechanical and thermal stability under operating conditions, good balance of water transfer, good transfer of gases to catalyst layer, etc [4]. At present, Nafion (a perfluorinated sulfonic acid (PFSA) ionomer) is widely used as the PEM material because of its good chemical stability, good mechanical properties, and high proton conductivity. But, on account of the high cost, high fuel permeability, and low ceiling operation temperature (<80 ℃) of Nafion, researchers are in search of new membrane [5]. Thus, the efforts have been put to develop alternative proton conductive materials with good thermomechanical stabilities and low cost [6, 7].Now, sulfonated poly (ether ether ketone) (SPEEK), a sulfonate-functionalized hydrocarbonpolymer, has gathered attention of researchers owing to its promising characteristics including thermal and mechanical strength, low price, simple preparation procedure and good film-forming capacity. The most recent research on SPEEK includesdiverse capabilities including biomedical materials [9-11], humidity sensors [12, 13], composite actuators [14], heterogeneous catalysts [15], shape memory polymers [16], dehydration of industrial gases and gas separation membranes [17, 18], water splitting electrodialysis devices [19], vanadium redox flow batteries [20], and fuel cells (microbial, direct methanol, alkaline exchange, and proton exchange membranes) [21-26]. The usage of an organic –inorganic composite membranes improved water retention capacity and mechanical properties as well as reduced fuel permeation. It can be an effective and convenient way to improve the performance of PEMs [27-28]. It is also reported that wood based fillers are incorporated into polymer matrices to achieve low manufacturing cost, moderately improved stiffness, decreased shrinkage and

increased resistance to abrasion and creep. The composites are environmental friendly because of their less dependence on non-renewable energy/material resources, less pollutant and greenhouse gas emissions, enhanced energy recovery, and end-of-life biodegradability [29–31].

In this context, as no one has attempted with wood polymer composite membrane for PEMFC we have tried with SPEEK / Artocarpus heterophyllus composite membrane so as to replace Nafion in the present work.

II. EXPERIMENTAL

A. Materials

The PEEK powder (150XF) was purchased from Victrex (England) with purity of 99.9% was used as received. Sulphuric acid (H2SO4) and 1-Methyl-2-pyrrolidone (NMP) both of AR grades supllied by E-Merck india Ltd. were used as received. The cost effective materials for fabricating a test fuelcell were purchased from Sainergy Fuelcell India Pvt Ltd (Such as Carbon Vulcan XC-72, Carbon Cloth and 40% Pt in Vulcan XC-72). In addition, a 60% Teflon dispersion purchased from Sigma Aldrich, USA and Isopropyl Alcohol (IPA- AR grade) was purchased from Rankem Chemicals for fabrication were used as received for fabrication.

B. Preparation of SPEEK/AH Composite Membrane Sulphonation of PEEK

A known quantity of PEEK powder was taken in a round bottom flask which was mixed with 150ml H_2SO_4 and stirred continuously for 6 hours using magnetic stirrer. The sulphonation reaction was arrested in an icebath. [32-33]. The resulting Sulphonated PEEK (SPEEK) fibres were washed in double distilled water to have neutral pH and later dried for 3 hours in hot air oven at 60°C.
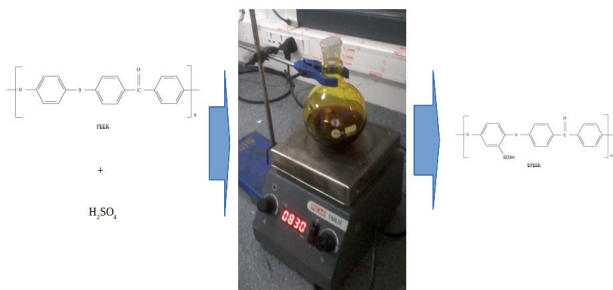

Fig.1: Sulphonation of PEEK

Preparation of Artocarpus heterophyllus Wood Powder (AH)

Heartwood nucleus of AH wood powder was collected from the available source and was shallow dried for 24 hours and subsequently dried in hot air oven at 60 °C so as to remove certain moisture present. Later the AH wood powder was made into a coagulated paste formation using deionised water as a solvent. As prepared paste like AH wood powder conserved in a petri dish placed in a hot air oven as it was placed earlier for the same 24 hour duration. The resultant product furtherance made into finassy using a pistle/mortor setup and this time it was kept in oven for 48 hours at 60degree C.

Preparation of SPEEK/AH Composite Membrane

Step.1 Process

The SPEEK was dissolved in NMP at ambient temperature and the mixture was stirred continuously for an hour. The homogenous solution so obtained was then filtered and cast onto a dry clean petri dish. The petri dish was so filled kept in oven at 60°C for 24hours. The membranes so prepared in this process were found to be pale brown in colour as shown.

Step.2 Process

The measured quantity of AH was dispersed in NMP and the solution was stirred for 2 hours. The AH dispersion so prepared was then added in drop by drop into the SPEEK NMP Binary solution and the resulting terinary mixture was stirred for 4 hours till it turned into homogenity. This homogeneous solution was cast onto a clean petri dish and dried in the Hot air oven at 60°C for slow evaporation of the solvent to avoid any fissures in the resulting membrane. After the complete evaporation, membranes were peeled off from the container and subsequently treated with 0.5N H_2SO_4, and washed with deionized water. A set of five different composites with varying concentrations of 99% SPEEK - 1%AH, 98%SPEEK-2%AH, 97% SPEEK-3%AH, 96%SPEEK-4%AH, 95%SPEEK- 5% AH, were prepared using the solvent casting technique. These prepared membranes were found to have 80-100 micron in thickness.

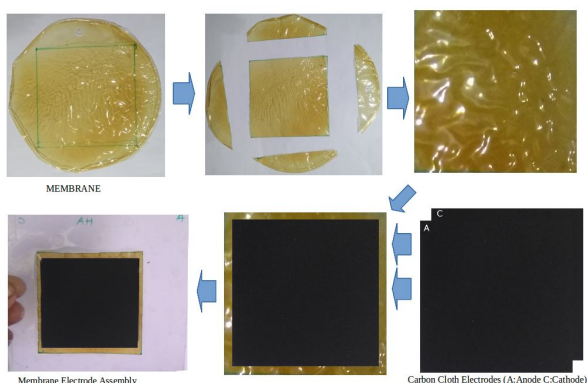### C. Fabrication of membrane electrode assembly(MEA)

Fig.2.MEA Preparation stages

The procedure for preparing a MEA adhered to standard protocols. [41]

  a. Purification of membrane
  b. Teflonization of porous carbon cloth
  c. Carbonization of the teflonized carbon cloth
  d. Catalyst layer first stage coating
  e. Catalyst layer second stage coating
  f. Hot pressing of the electrodes on the membrane

Purification of the Membrane

Purification of the membrane is very crucial and must be performed before the preparation of MEA. Initially, all membranes were allowed to boil in 3% H_2O_2 for 45 minutes which removed the impurities, if any, present on the surface of the membrane. It was then washed thoroughly with distilled water and boiled for 30 minutes in 10% H_2SO_4 to remove any inorganic impurities and to get the membrane in a complete protonated form. Finally, the membrane was washed with boiling water to remove any excess acid present on the surface of the membrane and later the membrane was dried.

Teflonization of the porous carbon cloth

For the teflonization process, a 60% Teflon dispersion in water available commercially was procured and was further diluted with deionised water in the ratio of 1:5. The carbon cloth was highly porous in nature and was dipped in the above dispersion for 30 seconds. Then placed in a muffle furnace at 350°C for a duration of 3 hours. The process of teflonization improve the hydrophobicity of the carbon cloth.

Carbonization of the teflonized carbon cloth

This is also called as the Gas Diffusion Layer (GDL). Initially Vulcan XC-72 (3mg/cm 2) is mixed with 3ml of deionised water and sonicated for 10 minutes. The sonication

was done to obtain a fine dispersion of the carbon particles. Then 2-3 ml of isopropyl alcohol (IPA) was added and sonicated again for 10 minutes. Finally, a drop of Teflon dispersion was added, mixed and immediately coated on the carbon cloth by means of a brush. The cloth was subsequently kept in a muffle furnace at 350°C for 3 hours.

Catalyst layer first stage coating

Anode

The catalyst used was Pt dispersed in carbon. For the first stage, the amount of Pt taken was 0.125 mg/cm^2 . The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then 1-2 drops of IPA was added and sonicated for another 10 minutes. Finally, one drop of Teflon dispersion was added, mixed with the help of a painting brush and coated immediately on the carbonized cloth. It was then heated in a muffle furnace at 350°C for a duration of 3 hours.

Cathode

The first layer of catalyst was coated as done for anode.

Catalyst layer second stage coating

Anode

For the second stage, the amount of Pt taken was 0.125 mg/ cm^2. The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then few drops of SPEEK solution were added and then coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It was then dried in a hot air oven at 80°C for 4 hours. The electrode obtained after drying could be used as the anode for the fabrication of the MEA.

Cathode

For the second stage, the amount of Pt taken was 0.375 mg/cm^2 . The required amount of the catalyst was weighed and mixed with 3 ml of water and sonicated for 10 minutes. Then few drops of SPEEK solution were added, mixed and coated immediately on the carbon cloth over the catalyst layer coated during the first stage. It was dried in an oven at 80°C for 4 hours. The electrode obtained was the cathode that can be used for the fabrication of the MEA.

Hot pressing of the electrodes on the membrane

On either side of the membrane, a solution of SPEEK in NMP was applied and the electrodes are placed on either side. It was hot pressed at 80°C for 45 seconds with a load of 0.5 tonnes. The two electrodes stuck onto the membrane after the hot pressing treatment. The resulting assembly was the Membrane Electrode Assembly (MEA). This MEA was used in the PEMFC for performance evaluation.

III. CHARECTERIZATIONS

Membrane Characterization

XRD measurements were performed using an Ultimate IV diffractometer of Rigaku, Japan. The dried samples were mounted on an aluminium sample holder. The scanning angle ranged from 10° to 80° at a scanning rate of 2° per min. All the spectra were taken at ambient temperatures (25 ± 2°C).   The IR spectra for the dried membranes were recorded with a Perkin Elmer / Spectrum 2 Diamond UATR FT-IR spectrometer for wave number 400 – 4000 cm^{-1}. The samples were dried at 100°C for an hour before recording the spectrum.TGA analysis is mainly carried out to determine the thermal stability of the composite membranes. The change in weight of the membrane with increase in temperature at a heating rate of 10°C/min in the range of the temperature between 30°C and 750°C is followed using a Thermo Gravimetric Analyzer SDT Q600 of TA Instruments, USA. All the runs were carried out under nitrogen atmosphere.
The surface morphology of the electrolyte membranes was analysed using SEM (Hitachi S – 3400 N). The samples were cut into sufficient size and sputter coated with gold to make the samples electro conductive. The samples were then analyzed under vacuum condition at an accelerating voltage of 10 KV.

Water Uptake

The amount of solvent intake by the membranes was studied. The dried membranes were weighed and soaked in water and methanol separately and allowed to get equilibrated at room temperature for 40 hours, above which the weight was constant. The swollen membranes were then immediately weighed after blotting the surface water and the values noted. The swelling degree was determined using the formula,

$$SW = \frac{M\,wet - M\,dry}{M\,dry}$$

where,
M wet =

Weight of wet membrane,

M dry =

Weight of dry membrane.

Ion exchange capacity (IEC)

The ion exchange capacity (IEC) indicates the number of milliequivalents of ions in 1g of the dry polymer. It was determined by titration method, repeated n times for confirmity. The membrane in its protonated form was weighed and then soaked in an aqueous solution containing a large excess of KCl in order to extract all the protons from the membrane. The electrolyte solution was then neutralized using a very dilute Na_2CO_3 solution of known concentration (0.01N). The EW (equivalent weight) values were calculated from the dry weight of the membrane divided by the volume and the normality of the Na_2CO_3 solution. The IEC values were expressed as number of meq. of sulphonic groups per gram of dry polymer. IEC was calculated using the formula,

$$IEC = \frac{Titer\ value\ (in\ ml) \times Normality\ of\ the\ titrant\ (Na_2CO_3)}{Weight\ of\ the\ dry\ polymer\ membrane\ (in\ grams)}$$

Proton Conductivity

The proton conductivity measurements were taken using an alternating current impedance spectroscopy device over a frequency range of 1-10^7 Hz with 50 - 500mV oscillating voltage using a Hioki 3532-50 LCR HiTester. Films having 1cm^2, sandwiched between two stainless steel block electrodes with ~3 kg/cm^2 pressure, were placed in an open, temperature-controlled cell. The films were previously hydrated by soaking in deionised water for 24 hours at room temperature. The conductivity σ of samples in the transverse direction were calculated from the impedance data, using the relationship

$$\sigma = \frac{d}{RS}$$

where, d and S are the thickness and face area of the membrane sample, respectively, and R found from the low intersection of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis.

Oxidative stability

For checking the durability of the electrolyte membranes, the following procedure was adopted. Initially a 4ppm ferrous ammonium sulfate in 3% H_2O_2 was freshly prepared and the temperature of the solution was maintained at 80°C. The electrolyte membrane with the dimension of 0.5cm 2 was cut and soaked in the solution. The time required for the physical disintegration of the membrane was noted down and reported.

Single Cell Fuelcell performance Test

Selected sample was subjected to testing in real time PEMFC environment with hydrogen gas as fuel. Standard fuel cell grade graphite plates and copper current collectors were used for this purpose. The output voltage and the current were measured with a research grade digital multimeter (CD800a of Sanwa,Japan with accuracy of ±0.7% with resolution of 0.1mV) under different resistances as loads

IV. RESULTS AND DISCUSSIONS

XRD studies

The XRD pattern of PEEK, SPEEK, AH and various composites of different membranes are shown in fig3. PEEK shows XRD peaks at 18.9º, 20.6º, 22.8º and 28.9º due to its semi-crystalline nature. These peaks are ascribed to the diffraction at (110), (111), (200) and (211) crystalline planes respectively. Introduction of SO_3H group reduces the crystallinity of PEEK due to its restriction imparted by functional groups in ordered packing of polymeric chains. Thus intensity of (110) peak is reduced in SPEEK with relative broadening and other crystalline peaks are not found in SPEEK due to disruption of crystalline structure and it becomes amorphous. [34,35] Diffraction peaks at 16.0° and 22.5° appear in the wood spectra, which originated from the crystalline region of the cellulose in the wood. [36] The broadness of its humps imply the amorphousity in wood powder. [37] . In the case of composite membranes this peak slowly gets diminished and a new peak appeared around 22º. These get broadened as a result the blended membrane become amorphous.
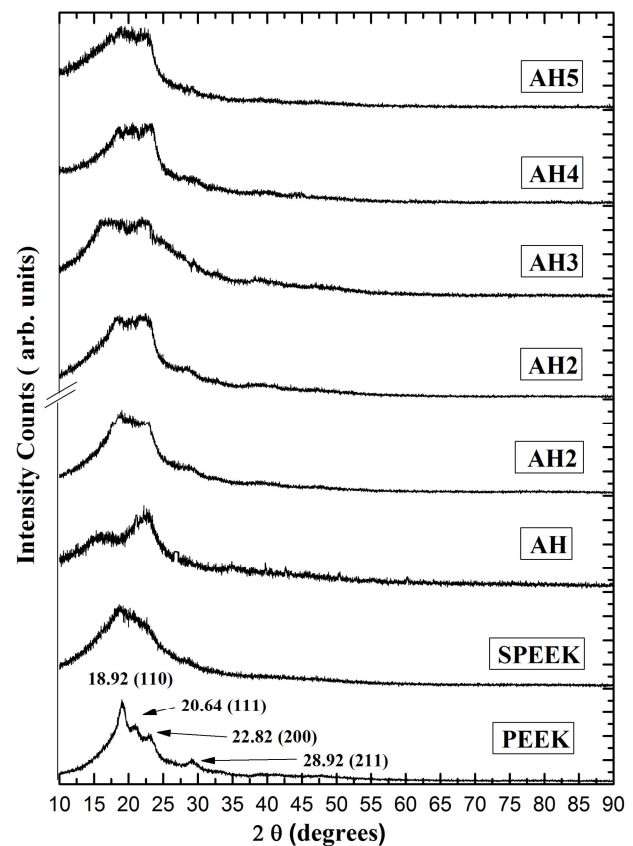

Fig.3. XRD pattern of virgin PEEK, SPEEK , AH, and SPEEK/AH composite membranes
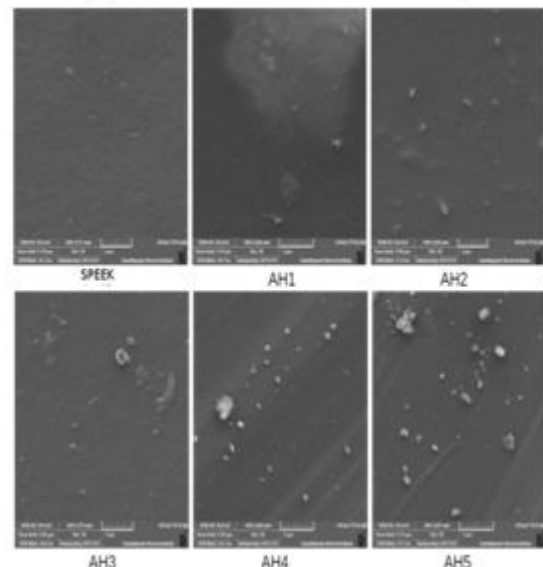
SEM Studies

Fig.4. SEM images of Virgin SPEEK, and SPEEK/AH composites of different concentrations

The SEM images of virgin SPEEK and SPEEK+SA composite membranes are given in fig4. All SEM images appear dense and homogenous indicating a uniform

distribution of Artocarpus heterophyllus in the polymer matrix. No fissures could be observed in the virgin as well as composite membranes. Usage of high boiling point solvent (202 °C) and evaporation of casted membranes at 80 °C paved the way for smooth membrane formation.
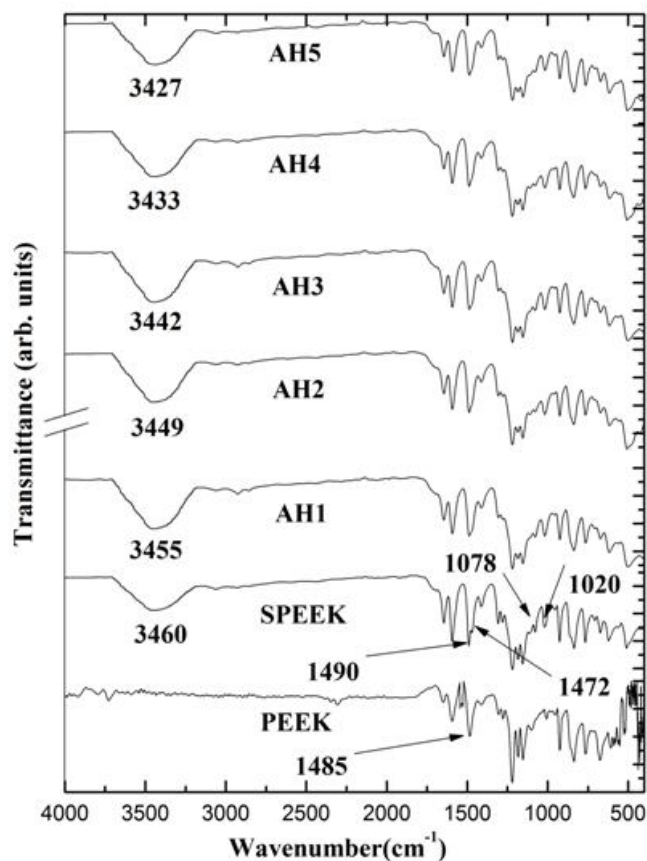
FTIR Studies

Fig.5. FTIR spectra of PEEK, SPEEK and SPEEK/AH composite membranes at different concentrations.

Fig.5 shows the comparative FTIR spectra of PEEK, SPEEK and the various composite membranes. The peak observed at 1485 cm^{-1} in PEEK is the aromatic C-C band, which is split into 1490 and 1472 cm^{-1} in SPEEK due to the new substitution from the sulfonation reaction. The new peaks observed at 1024 and 1080 cm^{-1} correspond to symmetric and asymmetric stretching vibration of the sulfonic acid group in SPEEK.[38,39]. It confirms sulphonation of PEEK. There is a significant broad peak at 3460 cm^{-1} in SPEEK assigned to OH vibration from sulphonic acid groups interacting with molecular water [40]. In the SPEEK composite membranes, the hydroxyl band is observed at 3460 cm^{-1} with a small shift in wavelength attributes to the effective hydrogen bonding interactions between SPEEK and the filler[41]. Most of the characteristic peaks of the filler are blocked due to the interference by the SPEEK matrix found highest percentages.

[42]. The peak between 1600 cm^{-1} and 1750 cm^{-1} are due to the vibration of carbonyl group of SPEEK. The peaks at 1050 cm^{-1} and 1100 cm^{-1} confirm the presence of O=S=O groups.

TGA Studies

The thermogram of SPEEK and various composite membranes are shown in fig.6 The thermogram of composite membranes are found to be similar to that of virgin SPEEK. A three stage degradation is observed for the electrolyte membranes. The first weight loss is observed between 80ºC and 150ºC. This weight loss may be attributed to the loss of physically and chemically adsorbed water. Even though the composite membranes exhibit a better water absorption capacity, the thermal energy available at temperatures over 120ºC is sufficient to break the interaction between water and wood material and thereby liberates water. However the weight loss extends upto 150ºC. The second major weight loss is between 230ºC and 350ºC. This may be reasoned be due to the liberation of sulphonic acid group attached with the polymer matrix. The third loss is found between 425ºC and 600ºC may be attributed to the degradation of the polymer matrix.
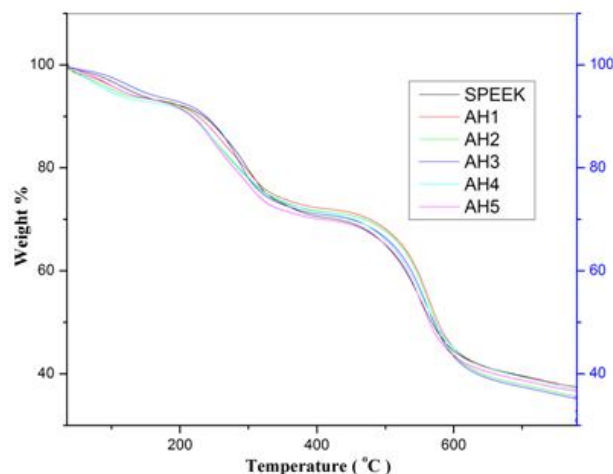

Fig. 6. TGA of Pure SPEEK and SPEEK/AH composite membranes.

Ion Exchange Capacity

The Ion- Exchange Capacity of pure SPEEK and SPEEK+AH membranes are given in table 1. It is observed that IEC of pure SPEEK is found to be 2.19 meq/g, and it might be due to the loading of AH which could enhance the magnitude of IEC . Consequently, the enhancement of IEC are found to increase gradually with increase in concentration of AH. This increasing trend may be due to the significant water absorbing capacity of the AH. Before observing the role of organic content in the composite membrane, it was presumed

that increase in organic content in the composite membrane would decrease the magnitude of IEC. But, it showed reverse trend, in empirical observations, that IEC magnitude started to increase with increase of it.

Table 1. Obsrved results of Pure SPEEK and its composite membranes

Sample	Test Values			
	IEC, meq/g	Water Absorption, wt%	Chemical Stability, min	Protonic Conductivity mS/cm
SPEEK	2.19	14.15	261	8.53
AH1	2.19	14.47	256	8.58
AH2	2.20	14.73	250	8.61
AH3	2.21	14.96	241	8.64
AH4	2.21	15.12	235	8.70
AH5	2.22	15.31	229	8.74

Water Absorption

The Table..1 Presents water absorption (wt%), chemical stability of samples pure SPEEK , AH1 (99wt%SPEEK+1wt% AH), AH2 (98wt%SPEEK+2wt% AH), AH3 (97wt%SPEEK + 3wt%AH),AH4 (96wt%SPEEK+4wt% AH) and AH5 (95wt%SPEEK+5wt% AH) respectively. It is noted that the water absorption of vifgin SPEEK is found to be 14.15 wt% whereas it is 15.31 against the sample AH5 wherein the maximum concentration of Artocarpus heterophyllus is present. This suggests that the water absorbing capacity is found to vary as a function of the concentration of Artocarpus heterophyllus This may be due to hydrophilic sulphonic acid group is mainly responsible for the water absorption. With increase in the content of wood powder, the net content of sulphonic acid group decreases, even then there is increase in the water absorbing ability. This may be ascribed to the greater water absorbing capacity of the wood powder.
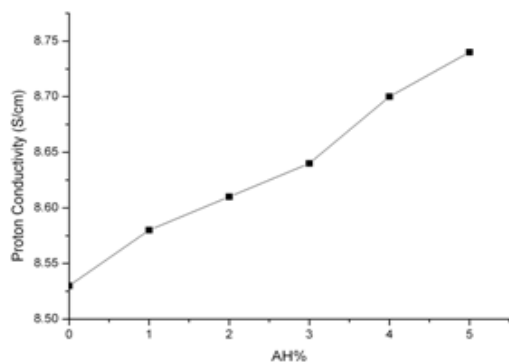
Proton Conductivity

Fig. 7. Proton conductivity at variation of AH concentratetion

The proton conductivity of SPEEK with various concentration of AH is given in the fig. The sulphonic acid group available in SPEEK is primarily responsible for the transportation of protons. The proton conductivity of the composite membranes are found to be in an increasing trend when compared to SPEEK. This clearly shows that the composite membranes are capable of transporting protons better than virgin SPEEK even though there is a decrease in the net sulphonic acid group with increase in the wood content. This inherent nature may be due to the increased water holding capacity of the composite membranes as compared to SPEEK.

Chemical stability

The experimental results of chemical stability of various electrolyte membranes were given in Table1. The hydrolytic stability of SPEEK was found to be 261 minutes. The oxidative stability of the composite membranes found to decrease with increase in the wood content. It was noted that increasing the composition of the wood content, the continuity in the polymer matrix was disturbed and hence there could be regions where breaking was relatively easy. This might be the reason for the decrease in the chemical stability of the composite membranes

Single cell performance

The prepared pure SPEEK and SPEEK-AH membranes are subjected to single-cell test in order to evaluate their suitability for fuel cell applications. Figure 10 displays the single-cell performance of fabricated composite membrane at room temperature at 30 °C. The open circuit voltage for the composite was observed to be 0.913V comparing to that of pure SPEEK 0.896V. The peak power density attained by SPEEK-AH composite 82 mWcm^{-2} which was comparatively higher than that of Pure SPEEK (76 mW cm -2). This result indicates that the prepared membrane could be used as potential candidate for PEMFC.
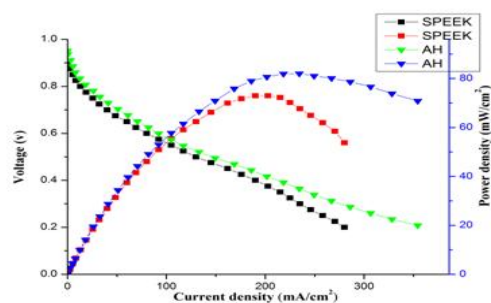

Fig.8. Single cell performance studies for virgin SPEEK and SPEEK/AH composite membranes

V. CONCLUSION

SPEEK/AH, a novel wood-polymer composite membrane is found to be a potential candidate replacing the Nafion for PEM fuel cell. All physical characterisations have well supporting the 5 wt% AH incorporated SPEEK matrix proved its suitability. Fabrication of the PEM fuel cell performance has also been confirming the same with good open circuit voltage and better power density as the prominent tentacles as membrane to be employed for PEMFC.

REFERENCES

[1] Yee RS, Zhang K, Ladewig BP (2013) The effects of sulfonated poly(ether ether ketone) ion exchange preparation conditions on membrane properties. Membranes 3:182–195

[2] F. Mirzaei, M. J Parnian, S. Rowshanzamir, Durability investigation and performance study of hydrothermal synthesized platinum-multi walled carbon nanotube nanocomposite catalyst for proton exchange membrane fuel cell. Energy 2017;138:696–705.

[3] S. Nunes, Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells.J. Membr. Sci. 2002;203:215–225.

[4] P. Sayadi, S. Rowshanzamir, M. J. Parnian, Study of hydrogen crossover and proton conductivity of self-. humidifying nanocomposite proton exchange membrane based on sulfonated poly (ether ether ketone).Energy 2016;94:292–303.

[5] Ishimoto T, Koyama M (2012) A review of molecular-level mechanism of membrane degradation in the polymer electrolyte fuel cell. Membranes 2:395–414

[6] Chi NT, Bae BC, Kim DJ (2013) Electro-osmotic drag effect on the methanol permeation for sulfonated poly(ether ether ketone) and Nafion 117 membranes. J Nanosci Nanotechnol 13:7529–7534

[7] Jung DW, Kim JH, Kim SH, Kim JB, Oh ES (2013) Performance enhancement of polymer electrolyte membrane fuel cells by dual layered membrane electrode assembly structures with carbon nano tubes. J Nanosci Nanotechnol 13:3650–3654

[8] Mohammad Javad Parnian , Fatemeh Gashoul , Soosan Rowshanzamir ; Studies on the SPEEK membrane with low degree of sulfonation as a stable proton exchange membrane for fuel cell applications ; Iranian Journal of Hydrogen & Fuel Cell 3(2016) 221-232

[9] Ouyang L., Zhao Y., Jin G., Lu T., Li J., Qiao Y., et al., "Influence of sulfur content on bone formation and antibacterial ability of sulfonated PEEK", Biomaterials 2016, 83:115.

[10] Montero J.F.D., Tajiri H.A., Barra G.O., Fredel M.C., Benfatti C.A.M., Magini R.S., et al. "Biofilm behavior on sulfonated poly(ether-ether-ketone) (sPEEK)", Materials Science and Engineering C. 2017, 70:456.

[11] Montero J.F., Barbosa L.C., Pereira U.A., Barra G.M., Fredel M.C., Benfatti C.A., et al. "Chemical, microscopic, and microbiological analysis of a functionalized poly-ether-ether-ketone-embedding antibiofilm compounds", Journal of Biomedical Materials Research Part A. 2016,104:3015.

[12] Zhuang Z., Qi D., Zhao C., Na H. "A novel highly sensitive humidity sensor derived from sulfonated poly(ether ether ketone) with metal salts-ion substitution", Sensors and Actuators B. 2016, 236:701.

[13] Zhuang Z., Li Y., Qi D., Zhao C., Na H. "Novel polymeric humidity sensors based on sulfonated poly (ether ether ketone) s: Influence of sulfonation degree on sensing properties", Sensors and Actuators B: Chemical. 2016, 242: 801.

[14] Tang Y., Xue Z., Xie X., Zhou X. "Ionic polymer–metal composite actuator based on sulfonated poly(ether ether ketone) with different degrees of sulfonation", Sensor and Actuators A. 2016, 238:167.

[15] Morizur V., Hector D., Olivero S., Desmurs J.R., Duñach E. "Metal Sulfonate Polymers as Catalysts for the Heterogeneous Acylation of Aromatic Derivatives", European Journal of Organic Chemistry. 2016, 2016:3126 .

[16] Shi Y., Yoonessi M., Weiss R.A. "High Temperature Shape Memory Polymers", Macromolecules. 2013, 46:4160.

[17] Azher H., Scholes C., Kanehashi S., Stevens G., Kentish S. "The effect of temperature on the permeation properties of Sulphonated Poly (Ether Ether) Ketone in wet flue gas streams", Journal of Membrane Science. 2016, 519:55.

[18] Xin Q., Zhang Y., Shi Y., Ye H., Lin L., Ding X., et al. "Tuning the performance of CO2 separation membranes by incorporating multifunctional modified silica microspheres into polymer matrix", Journal of Membrane Science. 2016, 514:73.

[19] Kwon S.H., Rhim J.W. "Study on Acid/Base Formation by Using Sulfonated Polyether Ether Ketone/ Aminated Polysulfone Bipolar Membranes in Water Splitting Electrodialysis", Industrial & Engineering Chemistry Research. 2016, 55:2128.

[20] Dai J., Teng X., Song Y., Jiang X., Yin G. "A super thin polytetrafluoroethylene/sulfonated poly(ether ether ketone) membrane with 91% energy efficiency and high stability for vanadium redox flow battery", Journal of Applied Polymer Science. 2016, 133:43593.

[21] Gong C., Zheng X., Liu H., Wang G., Cheng F., Zheng G., et al. "A new strategy for designing high- performance sulfonated poly(ether ether ketone) polymer electrolyte membranes using inorganic proton conductor-

functionalized carbon nanotubes", Journal of Power Sources 2016, 325:453.

[22] Sadrjahani M., Gharehaghaji A.A., Javanbakht M. "Aligned Electrospun Sulfonated Polyetheretherketone Nanober Based Proton Exchange Membranes for Fuel Cell Applications", Polymer Engineering and Science. 2016.

[23] Yin Y.H., Wang H.Y., Cao L., Li Z., Li Z.Y., Gang M.Y., et al. "Sulfonated poly(ether ether ketone)-based hybrid membranes containing graphene oxide with acid- base pairs for direct methanol fuel cells", Electrochimica Acta. 2016, 203:178.

[24] He S., Lin Y., Ma H., Jia H., Liu X., Lin J. "Preparation of sulfonated poly(ether ether ketone) (SPEEK) membrane using ethanol/water mixed solvent". Materials Letters. 2016, 169:69.

[25] Deuk Ju Kim C.H.P., Sang Yong Nam. "Characterization of a soluble poly(ether ether ketone)anion exchange membrane for fuel cell application", International Journal of Hydrogen Energy. 2016, 41:7649.

[26] Elangovan M., Dharmalingam S. "Scaleup Suitability of Sulfonated Polyether Ether Ketone Membrane- Based Microbial Fuel Cell", Environmental Progress & Sustainable Energy. 2016, 35:80.

[27] T. Chakrabarty, A.K. Singh, V.K. Shahi, Zwitterionic silica copolymer based crosslinked organic–inorganic hybrid polymer electrolyte membranes for fuel cell applications. RSC Adv. 2012;2:1949-1961.

[28] D.S. Kim, H.B. Park, J.W. Rhim, Y.M. Lee, Preparation and characterization of crosslinked PVA/SiO2 hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications. J. Membr.Sci. 2004;240:37–48.

[29] Selke SE, Wichman I (2004) Wood fiber/polyolefin composites. Composite Part A 35:321–326

[30] Joshi SV, Drzal LT, Mohanty AK, Arora S (2004) Are natural fiber composites environmentallysuperior to glass fiber reinforced composites? Composite Part A 35:371–376

[31] Li Q, Matuana LM (2003) Effectiveness of maleated and acrylic acid-functionalized polyolefincoupling agents for HDPE-wood-flour composites. J Thermoplas Compos Mater 16(6):551–564

[32] S.M.Javiad Zaidi; Arabian journal for Science and Engineering., 28(2B), 185 (2003)

[33] S.Guhan; Development of Blends and Composites of SPEEK as Electrolyte Membranes for Fuel Cells,PhD dissertation, Anna University, India, (2011)

[34] S.Banerjee, K Kar; Synergistic Effect of aluminium phosphate and tungstophosphoric acid on the physiochemical properties of sulfonated poly ether ether ketone nanocomposite membrane; J. Poly. App. Sc. , 42952 (2016)

[35] SG Adoor, SD Bhat, DD Dionysiou, MN Nagagouda, TM Aminabhavi, RSC Adv. 4, 52571-52582(2014)

[36] Islam, M. S., Hamdan, S., Jusoh, I., Rahman, M. R. & Ahmed, A. S. The effect of alkali pretreatment on mechanical and morphological properties of tropical wood polymer composites. Mater. Design. 33, 419–424 (2012).

[37] A Jain, S Jayaraman, M Ulaganathan, R Balasubramanian, V Aravindan, MP Srinivasan, S Madhavi ; Electrochimica Acta228:131-138 (2017)

[38] S. S. Mohtar, A. F. Ismail, and T. Matsuura, Journal of Membrane Science, 371, 10 (2011).

[39] Sangki Park and Hansung Kim, Preparation of a Sulfonated Poly(ether ether ketone)-Based Composite membrane with Phenyl Isocyanate Treated Sulfonated Graphene Oxide for a Vanadium Redox Flow Battery, Journal of The Electrochemical Society, 163 (10) A2293-A2298 (2016)

[40] P Xing, GP Robertson, MD Guiver, SD Mikhailenko, K Wang, S. Kaliaguine; Synthesis and   Characterization of sulphonated poly(ether ether ketone) for proton exchange membranes; J. Membr. Sc. 229(95-106) (2003)

[41] Hye-Ri Jang , Eun-Sil Yoo , Ramanujam Kannan, Jong-Suk Kim, Kieseung Lee,Dong Jin Yoo ; "Facile tailor-made enhancement in proton conductivity of sulfonated poly(ether ether ketone) by graphene oxide nanosheet for polymer electrolyte membrane fuel cell applications" ; Colloid Polym Sci., 295(6), pp 1059–1069 (2017)

[42] H Dogan, E Yildiz, M Kaya and T Y Inan ; Sulfonated carbon black-based composite membranes for fuel cell applications ;Bull. Mater. Sci., Vol. 36, No. 4, pp. 563–573, (2013).