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Sulphonated PEEK-Tectona Grandis Based Composite Membranes for PEM Fuelcells

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ABSTRACT

Sulphonated Poly Ether Ether Ketone (SPEEK) – Tectona grandis (TG) composite membranes have been prepared by varying TG from 0%, 1%, 2%, 3%, 4% and 5% while varying polymer content 100%, 99%, 98%, 97%, 96% and 95% by solution casting technique at 80°C environment. The obtained films were subjected to Ion Exchange Capacity (IEC), Water Absorption (WA), Chemical Stability (CS), Protonic Conductivity (PC) with view to understand the compatibility for their utility in PEMFuelcell application. TG5(SPEEK 95wt% + AI 5wt%) has maximum IEC, WA, conductivity and minimum CS compared to pure SPEEK. This may be reasoned that maximum WA accounted for IEC only propel for enhanced protonic transport mechanism. The FTIR studies confirms the Sulphonation of PEEK and complexation of SPEEK with TG. SEM shows the surface morphology of pure SPEEK and SPEEK/TG composite membranes, It is observed that beyond 5 weight% dispersion in SPEEK matrix, no free standing membrane is obtained may be due to immiscibility of TG with SPEEK. XRD studies on composite membranes showed semi-crystalline PEEK into amorphous membrane. TGA studies weight loss and there is no significant weight loss up to 230 °C. In PEMFC, the operational temperature is very well below that. MEA prepared with pure SPEEK as well as SPEEK/TG5 membranes and subjected to realtime PEMFC testing which resulted in better OCV as well as power density.
Keywords : Polymer Electrolyte Membrane Fuelcell, SPEEK/TG composite, Proton conductivity, Water Absorption, Realtime PEMFC test.

I. INTRODUCTION

The SPEEK based electrolytes for PEMFCs have revolutionised its end utility in fuelcells in electrochemical energy domain that impecably a promising green route accomplishments for fulfilling the generation of electricity, water and heat by an instil lucid reaction involving hydrogen as a fuel and oxygen as oxident. The PEMFCs due to their eventual applications such as high efficiency, low pollution and the quick start time [1-3] gearsup and marks fuelcells as a clean an ecofriendly energy conversion systems and hitherto appealing and revolutionalising the quantum of applications during the past decades [4-5].

As far as the commercialisation of fuelcells is concerned, Nafion based membrane invokingly prevails a well defined prescribed property accomplishments in terms of its viablity to fuelcells [6-7]. Albeit such inherent featuring properties it delves into certain discrepencies preferably its high cost, and drop in proton conductivity at high temperatures and prevailing the flourine in backbone and the dependence of proton conductivity as a function of water uptake and so on [8]. Thus a search for an alternative eco friendly with cost-effectiveness and platforming its performance at elevated temperatures[9-13] have eventually seeking polymer membranes texturing with aromatic hydrocarbons has been explored. [14-16]. With reference to the hydrocarbon polymers available, SPEEK has got its immense suitability replacing the Nafion (has testified which got rolled on with different electrochemical and mechanical properties) propelling the dynamism of SPEEK research has been ushered up in order to highly extend the scientific concreteness of the electrolyte membranes based on the SPEEK as a host with very appealing natural wood cellulose powder as an additive has been attempted with the conviction of facilitating good protonic transport mechanism as the basic requisite of an electrolyte membrane for fuelcells performance.[17,18] In askance tailoring of the SPEEK as a host texturing with the wood cellulose have been attempted as a ecofriendly membrane against Nafion in present work.

II. METHODS AND MATERIAL

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/TG Composite Membrane

B.1. 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. [19-20]. 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.

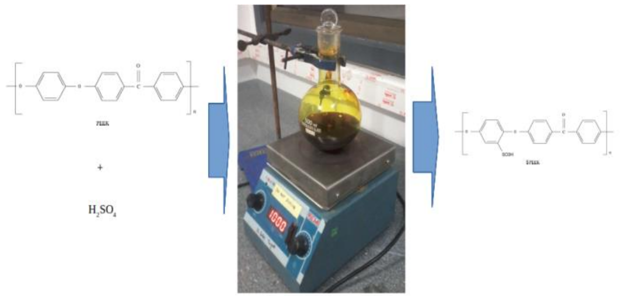

Figure 1. Sulphonation of PEEK

B.2. Preparation of Tectona grandis(TG) Wood Powder

Heartwood nucleus of TG wood powder was collected from the available source and was shallow dried for 24 hours and subsequently dried in hot air oven at 60 degree C so as to remove certain moisture present. Later the TG wood powder was made into a coagulated paste formation using deionised water as a solvent. As prepared paste like TG wood powder conserved in a petri dish placed in an 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.

B.3. Preparation of SPEEK/TG 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 on to 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 TG was dispersed in NMP and the solution was stirred for 2 hours. The TG 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%TG, 98%SPEEK-2%TG, 97% SPEEK-3%TG, 96%SPEEK-4%TG, 95%SPEEK- 5% TG, were prepared using the solvent casting technique. Thus prepared membranes were of 80-100 μ in thickness

B.4.Fabrication of membrane electrode assembly(MEA)

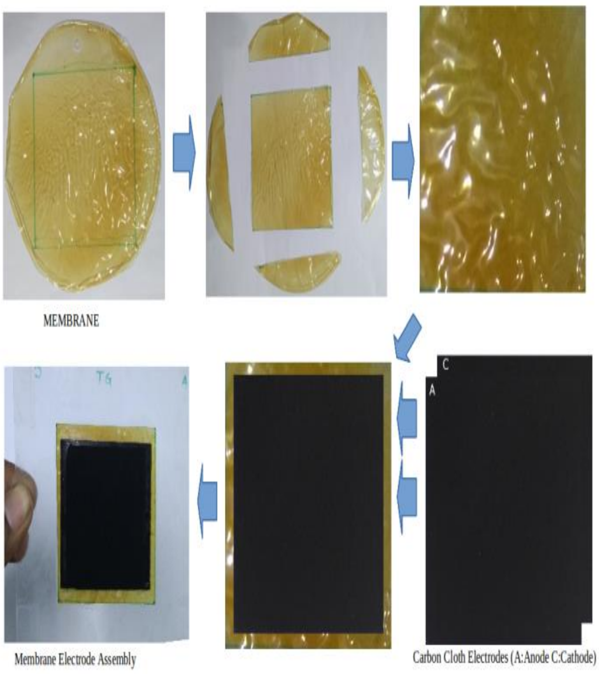

Figure 2. MEA Preparation stages

The procedure for preparing a MEA adhered to standard protocols [28].

a. Purification of membrane

b. Teflonization of porous carbon cloth

c. Carbonization of the teflonized carbon cloth

d. Catalyst layer first stage coating

d. Catalyst layer second stage coating

f. Hot pressing of the electrodes on the membrane

a. 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.

b. 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 soaked carbon cloth was placed in a muffle furnace at 350°C for 3 hours. The process of teflonization improve the hydrophobicity of the carbon cloth.

c. 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 carbonparticles. Then 2-3 ml of isopropyl alcohol 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 then kept in a muffle furnace at 350°C for 3 hours.

d. 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 3 hours.

Cathode

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

e. 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 1-2 drops of SPEEK solution was 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 was 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 could be used for the fabrication of the MEA.

f.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. The above MEA was used in the PEMFC for performance evaluation.

C. Characterizations

C.1. 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. 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.

C.2. 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 suddenly 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.

C.3. 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. 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 is calculated using the formula,

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

C.4. Proton Conductivity

The proton conductivity measurements were taken using an alternating current impedance spectroscopy device over afrequency 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 were calculated in the transverse direction 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 derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis. The impedance data were corrected for the contribution from empty and short circuited cell.

C.5. 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. The reaction is expected to occur by free radical mechanism.

C.6. Single Cell Fuelcell performance Test

Performance evaluation

Selected sample was subjected to testing in real time PEMFC environment with hydrogen gas as fuel. Fuelcell assembly and I-V performance was carried out at Amrita lab. 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 digital multimeter (CD800a of Sanwa, Japan with accuracy of ±0.7% with resolution of 0.1mV) under different resistances as loads.

III. RESULTS AND DISCUSSION

XRD studies

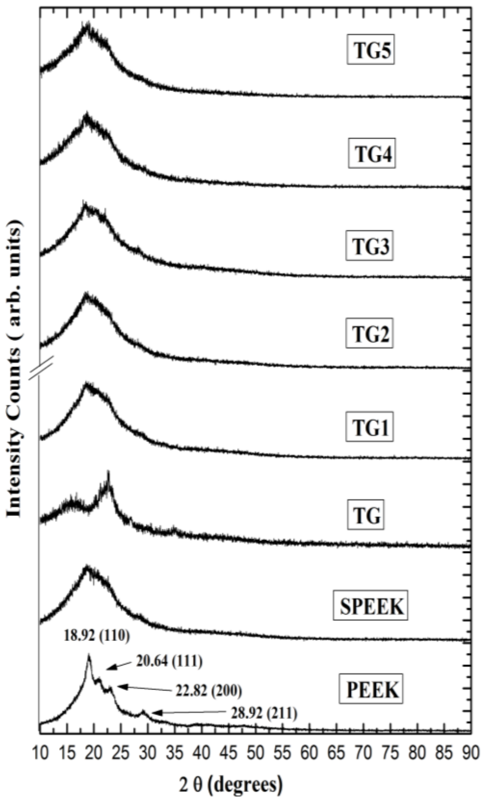

Figure 3. XRD pattern of virgin PEEK, SPEEK, TG and SPEEK/TG composite membranes

The XRD pattern of PEEK, SPEEK, TG and various composites of different membranes are shown in figure 3.PEEK shows XRD peaks at 18.7º, 20.6º, 22.6º and 28.6º due to its semi-crystalline nature. These peaks can be ascribed to the diffraction at (110), (111), (200) and (211) crystalline planes of PEEK, respectively. Introduction of SO_3H group reduces the crystallinity of PEEK due to restriction imparted by functional groups in ordered packing of polymeric chains. Thus intensity of (110) peak is reduced in SPEEK accompanying with relative broadening. Other crystalline peaks are not observed in SPEEK due to disruption of crystalline structure and becomes amorphous. [21,22] 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 [23]. The broadness of the humps implies the amorphousity in teak wood powder. [24] In the case of composite membranes the above said peak slowly diminishes and a new peak develops at around 22º. Both together broadened the peak and the blended membrane become amorphous. Absence of this peak in the case of composite membranes indicate an increase in the amorphous nature.

SEM studies

The SEM images of virgin SPEEK and SPEEK+TG composite membranes are given in fig.4. All the SEM images look dense, clear and homogenous indicating a uniform distribution of Tectona grandis in the polymer matrix. No fissures could be observed in the virgin as well as composite membranes. This is due to the use of high boiling point solvent used for casting purpose. During the membrane formation the solvent is evaporated at a very slow rate so that the continuity of the polymer matrix is maintained. The solvent is evaporated at a temperature of 80ºC even though the boiling point of the solvent is 202ºC.

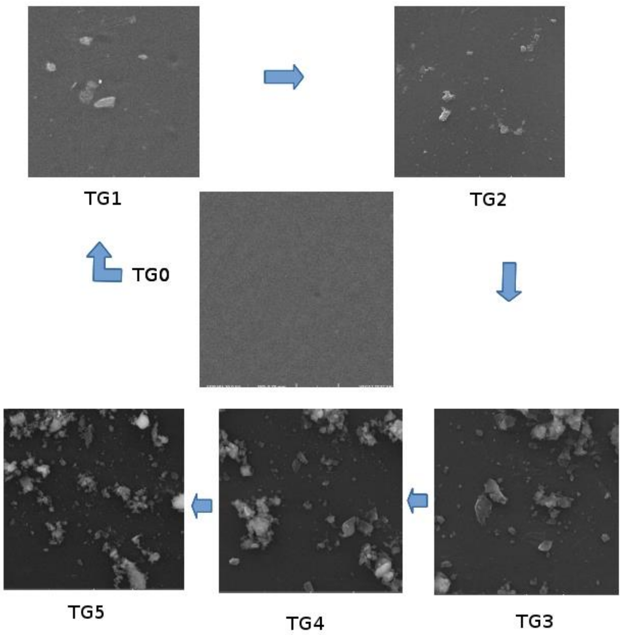

Figure 4. SEM images of pristine SPEEK, and SPEEK/TG composites.

FTIR studies

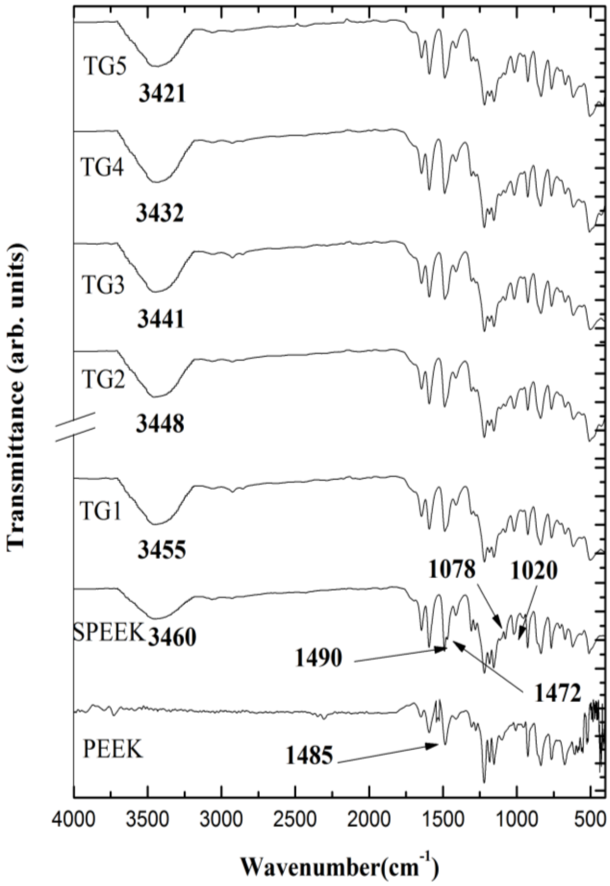

Figure 5.FTIR spectra of PEEK, SPEEK and SPEEK/TG composite membranes.

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 [25,26]. There is a significant broad peak at 3460 cm^{-1} in SPEEK is assigned to OH vibration from sulphonic acid groups interacting with molecular water [27]. 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 [28]. Most of the characteristic peaks of the filler are blocked due to the interference by the SPEEK matrix even though in the highest percentages [29]. The peak between 1600 cm^{-1} and 1750 cm^{-1} could be due to the vibration of carbonyl group of SPEEK. Moreover the peaks close to 1050 cm^{-1} and 1100 cm^{-1} confirm the presence of O=S=O groups. Thus sulphonation is confirmed in the PEEK back bone.

TGA studies

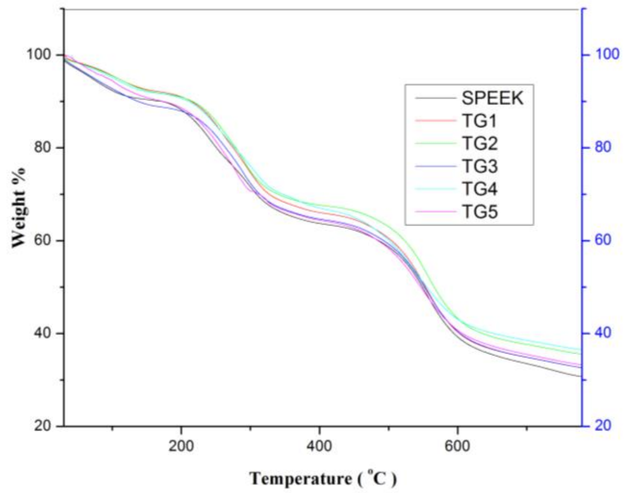

Figure 6. TGA of pristine SPEEK and SPEEK/TG composite membranes.

The thermogram of SPEEK and various composite membranes are shown in fig.6. The thermogram of the composite membranes are found to be similar to that of 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 there by liberates water. However the weight loss extends up to 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.

Ion Exchange Capacity(IEC)

The Ion- Exchange Capacity of pure SPEEK and SPEEK+Tectona grandis membranes are given in Table 1. It is observed that IEC of pure SPEEK is found to be 2.17 meq/g, and it may be due to the loading of Tectona grandis which can enhance the magnitude of IEC. Consequently, the enhancement of IEC are found to increase gradually with increase in concentration of Tectona grandis. This increasing trend may be due to the significant water absorbing capacity of the Tectona grandis. 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. Results of Pure SPEEK and its composite

Sample	Test Values			
	IEC meq /g	Water Absorption wt%	Chemical Stability min	Protonic Conductivity mS/cm
SPEEK	2.16	14.21	250	8.59
TG1	2.16	14.31	239	8.60
TG2	2.17	14.40	231	8.64
TG3	2.17	14.39	226	8.65
TG4	2.17	14.40	214	8.69
TG5	2.18	14.45	207	8.72

Water Absorption

The Table.1 presents water absorption (wt%), and Hydrolytic stability of pure SPEEK and its composites. It is noted that the water absorption of SPEEK is found to be 14.21 wt% whereas it is 14.45 against the sample TG5 wherein the maximum concentration of Tectona grandis is present. This suggests that the water absorbing capacity is found to vary as a function of the concentration of Tectona grandis. The 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 due to the greater water absorbing capacity of the wood powder.

Proton Conductivity

The proton conductivity of SPEEK with various concentration of Tectona grandis is given in the fig7. 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 peculiar nature may be due to the increased water holding capacity of the composite membranes as compared to SPEEK.

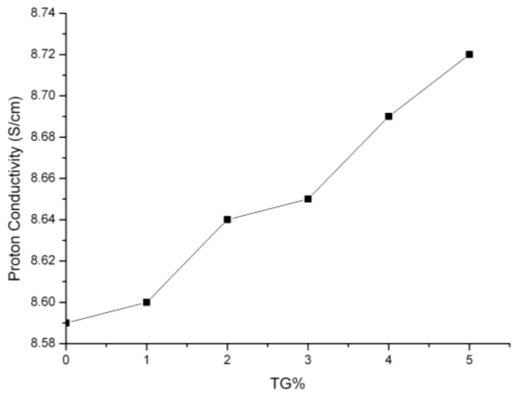

Figure 7. Proton conductivity at variation of TG concentration

Oxidative Stability

The experimental results of hydrolytic stability of various electrolyte membranes were given in Table1. The hydrolytic stability of SPEEK is found to be 250 minutes. The oxidative stability of the composite membranes decreases with increase in the wood content. As we increase the composition of the wood content, the continuity in the polymer matrix is disturbed and hence there can be regions where breaking is relatively easy. This may be the reason for the decrease in the hydrolytic stability of the composite membranes.

Single Cell Performance

The prepared pure SPEEK and SPEEK-TG membranes are subjected to single-cell test in order to evaluate their suitability for fuel cell applications. Fig.8 displays the single-cell performance of fabricated composite membrane at room temperature 30 °C. The open circuit voltage for the composite is observed to be 0.911V comparing to that of pure SPEEK at 0.896V. The peak power density attained by SPEEK-TG composite is 81 mWcm^{-2}, which is comparatively higher than that of Pure SPEEK (76 mWcm^{-2}). This result indicates that the prepared membrane can be used as potential candidate for PEMFC.

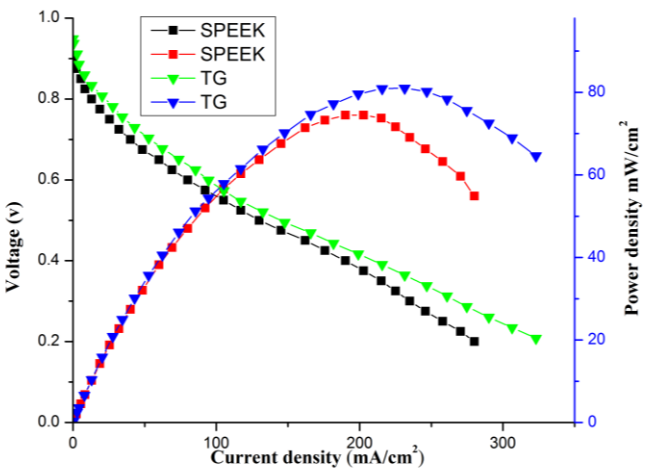

Figure 8. Single cell performance studies for virgin SPEEK and SPEEK/TG composite membranes

IV. CONCLUSION

The results show that SPEEK-TG composite membranes are excellent candidates as electrolyte membranes for fuel cell applications owing to the high stability, improved proton conductivity and appreciable thermal stability. From the various studies it is observed that the composite membrane labelled as TG-5 is found to be ideal for fuel cell application. The performance of the membrane is also studied and found to be on par with the commercial membranes.

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