

Development of Sulfonated Poly(ether ether ketone)/Zirconium Titanium Phosphate Composite Membranes for Direct Methanol Fuel Cell

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ABSTRACT: The present work addresses the development of economic membrane material with superior proton conductivity and less methanol crossover. Sulfonated poly(ether ether ketone) (SPEEK) composite membranes with various loading of zirconium titanium phosphate (ZTP) have been prepared by solution casting method. The structural and thermal properties of the ZTP powder are evaluated using X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area measurement, Fourier transform infrared spectroscopy (FTIR), and Thermo gravimetric analysis (TGA). The produced composite membranes are also characterized by evaluating the ion exchange capacity (IEC), water uptake, methanol uptake, thermal stability, proton conductivity, and methanol crossover as a function of ZTP loading. The proton conductivity of composite membrane is fourfold higher

than that of the pure SPEEK membrane and also increases with an increase in the ZTP loading. The methanol permeability of the composite membrane containing 15% ZTP decreases by 264% (and 21%) when compared with pure SPEEK (and commercial Nafion 117 membrane). Over all, the selectivity of the SPEEK/ZTP composite membrane is found to be 15- and 3-fold higher than the pure SPEEK membrane and Nafion 117 membrane, respectively. Hence, the synthesized SPEEK composite membrane could be utilized as low cost alternative for the high cost commercial membranes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: E45–E56, 2012

Key words: SPEEK; ZTP; composite membrane; methanol permeation; DMFC

INTRODUCTION

Direct methanol fuel cell (DMFC) is suitable for portable devices (cell phones, laptops) or transportation applications (cars, trucks, and buses) owing to its lower weight, high energy density, simple design, ease of handling a liquid fuel (easy storage of methanol, no reformer required), low emissions, and low operating temperatures.^{1–3} The proton exchange membrane (PEM) material is a key component of the DMFC for transferring protons from the anode to the cathode as well as providing a barrier to methanol crossover between the electrodes. Nowadays, perfluorinated ionomers (PFI) such as Nafion[®], Aciplex[®], and Dow[®] are widely used as membrane material in DMFC because of their good chemical and physical stability as well as high proton conductivity. In spite of the outstanding properties of these membranes, they are expensive (US \$800–2000 m⁻²) due to the complicated production process and also suffer from serious drawbacks, such as high methanol permeation and loss of conductivity at tempera-

ture above 80°C.^{4,5} In particular, high methanol diffusion leads to poisoning of the catalyst and reduction of the electrical performance and the fuel efficiency during the DMFC operation. In view of this, the development of inexpensive membranes (which possess high conductivity and low methanol permeability) based on nonfluorinated ionomers as alternative to PFI has gained much attention and turned to be the most challenging in the field of membrane community in the last few years.^{6,7}

In recent years, several studies have been carried out on aromatic polymers such as polyethersulfone (PSU), poly(ether ether ketone) (PEEK), polyphenylquinoxaline (PPQ), and polybenzimidazole (PBI) to be possible substitutes for PFI provided that a charge group such as sulfonic is introduced into the structural unit.^{8–13} Among the aforementioned polymers, PEEK is considered to be the most interesting polymer due to its commercial availability, good thermal, chemical, and mechanical properties. The PEEK can be converted to sulfonated poly(ether ether ketone) (SPEEK), a proton conducting polymer, by the electrophilic substitution of sulfonic acid groups in the polymer backbone.¹⁴ The proton conductivity of SPEEK is directly related to the degree of sulfonation (DS) which is controlled by reaction time, temperature of sulfonation process, and

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concentration of sulfonating agent. Although SPEEK exhibits various advantages to be used in PEM fuel cells, high sulfonation degree resulting in the relatively high methanol permeability has limited its applications.¹⁵ There have been many attempts to reduce the methanol permeability through the PEMs, which are: (1) modify the membranes surface to block methanol transport, (2) control the size of the transport channels of protons, (3) explore composite polymer materials, etc.

Thus, the composite membrane is one of the alternatives in tackling problems faced by perfluorinated and polymer membrane. It is very interesting because many of the inorganic additives used are able to operate at relatively higher temperatures than the pure polymers. Some of the possible advantages of incorporating inorganic compounds into composite membrane include enhanced proton conductivity, water retention at high temperature, reduce the methanol permeability and at the same time, it act as a mechanical support. Recently, a series of organic–inorganic composite membranes using SPEEK as a polymer matrix have been investigated for DMFCs, for example, the composite membrane of SPEEK with (i) heteropolyacid^{16–18}; (ii) zirconium phosphate^{19,20}; (iii) silicon oxide (SiO₂), titanium oxide (TiO₂), and zirconium oxide (ZrO₂)^{21,22}; (iv) boron phosphate (BPO₄)²³ and (v) layered silicate materials.²⁴ The simplest approach for the preparation of these composite membranes is to mix solid powders of fast proton conductors with polymer solution, and casting the resultant mixture for membrane formation.

Mikhailenko et al.²³ observed a conductivity of 0.05 S cm⁻¹ at 160°C and fully hydrated conditions while Zaidi et al.¹⁶ reported 0.1 S cm⁻¹ above 100°C with thermal stability up to temperatures above 250°C in SPEEK/heteropolyacid (HPA) membranes. Though membranes loaded with HPAs showed high water uptake and good proton conductivity, the HPAs tend to dissolve in water present in the membrane due to its high solubility. To avoid dissolution, HPAs were loaded onto MCM-41 (mesoporous silica).²⁵ Krishnan et al.²⁶ have reported a threefold increase in the conductivity of SPEEK with 50% loading of Zr[sulfophenylphosphonate (SPP)]. They have also introduced boron phosphate, prepared by an *in situ* sol–gel process, to SPEEK and showed almost sixfold increase in the conductivity when compared to pure SPEEK membranes.²⁷ Licocia et al.²⁸ prepared a modified silane bearing sulfonic acid functionality (sulfonated diphenylsilanediol, SDPSD) and made a SPEEK composite membrane with promising conductivity at 120°C. Nunes et al.²⁹ claimed a remarkable reduction of the methanol and water permeability by inorganic modification of SPEEK by *in situ* hydrolysis of different

alkoxides of Si, Ti, and Zr. The above extensive review clearly indicates that the incorporation of inorganic additives into the SPEEK polymer matrix improves the properties of the fuel cell membrane. To our best knowledge, no work has been reported on the synthesis of novel SPEEK composite membrane based on zirconium titanium phosphate (ZTP) before.

Therefore, this article addresses the preparation of SPEEK/ZTP composite membranes with different ZTP content in SPEEK polymer matrix. In addition, the influence of ZTP loading on the properties of the composite membrane such as thermal stability, water uptake, methanol uptake, proton conductivity, and methanol permeability is also investigated.

EXPERIMENTAL

Materials

Gatone PEEK (grade 5300p) used in this work was gifted by Solvay Specialities Pvt. Mumbai, India. Sulfuric acid (98%) (MERCK, Mumbai, India), dimethylacetamide (DMAc) (Spectrochem Pvt., Mumbai), zirconium oxychloride (ZrOCl₂·8H₂O) (LOBA Chemie, India), sodium dihydrogen orthophosphate GR (NaH₂PO₄·2H₂O) (LOBA Chemie, India), and titanium tetrachloride (TiCl₄) (LOBA Chemie, India) were obtained and used without further purification.

Sulfonation of PEEK

PEEK polymer (6 g) was dried in an air oven at 80°C for 12 h, prior to sulfonation. The powder was then added to 100 mL of concentrated sulfuric acid (98%) very slowly, with continuous stirring on a stirrer plate. Care was taken to prevent formation of lumps as they result in non-uniform sulfonation of PEEK. After addition of PEEK, the reaction mixture was refluxed at controlled temperature (55°C) for desired reaction time (1, 2, and 3 h) in air atmosphere. After a prescribed time, the reaction vessel was immersed in an ice bath to stop the reaction. Then the SPEEK polymer was precipitated out by pouring the polymer solution in deionized water (maximum temperature of 5°C) through a funnel with a very fine bore yielding thin strands of SPEEK. The SPEEK strands were filtered and washed thoroughly with Millipore water to remove excess acid until the pH of the wash solution was neutral. After that, the SPEEK polymer was dried at room temperature for 1 day and finally dried in a vacuum oven at 80°C for 6–8 h.

Synthesis of zirconium titanium phosphate

A solution containing 0.1M TiCl₄ and 0.1M ZrOCl₂·8H₂O in 10% w/v H₂SO₄ (100 mL) was prepared. To the above solution, 0.2M (200 mL) NaH₂PO₄·2H₂O was added drop wise, approximately 1 mL min⁻¹

with continuous stirring at room temperature, and a white precipitate was formed immediately. On complete precipitation, the gel obtained was stirred for a further 5 h. It was then kept in contact with mother liquor overnight. The resultant solution was filtered and washed with deionized water till the removal of chloride ions. The washed sample was dried at room temperature for 2 days. Then the dried sample was grinded and sieved using 45 mesh to obtain a fine powder ZTP.³⁰

Preparation of SPEEK/ZTP composite membrane

Solution casting method, which is generally used for making dense polymeric membranes, was adopted in preparing composite membranes. A known quantity of SPEEK (synthesized at 2-h reaction time) was dissolved in DMAc under stirring at room temperature. After complete dissolution of the polymer, a required amount of ZTP (5, 10, and 15 wt % with respect to polymer) was added. Then the suspension was stirred for 2 h, treated in an ultrasonic bath for 1 h to disperse the particles fully into the mixture and finally again stirred for 1 h using magnetic stirrer. Then the resultant mixture of known quantity was cast onto a glass plate. The glass plate was left for 24 h in atmosphere and then placed in oven at 80°C for 5 h to obtain composite membrane. After cooling down to room temperature, the resultant membranes were peeled from the glass after immersion in deionized water for 30 min. For comparison purpose, the pure SPEEK membrane (without ZTP) was also prepared using the same procedure described above.

Characterization

Ion exchange capacity

The ion exchange capacity (IEC) of SPEEK polymers and membranes, which is a measure of the number of counter ions exchangeable in SPEEK, was measured at room temperature as function of sulfonation reaction time. First, the membrane in acid form was transferred into the sodium form by immersing into 50 mL of 1.0M NaCl solution for 48 h to liberate H⁺ ions (the protons (H⁺) of the sulfuric acid group were replaced by sodium (Na⁺) ions). Then the exchanged protons (H⁺) were titrated with 0.01M NaOH solution using phenolphthalein as an indicator.^{31–33} The titrated IEC was determined from the following formula,

$$\text{IEC}(\text{meq/g}) = \frac{\text{Consumed NaOH} \times \text{molarity of NaOH}}{\text{weight of dried membrane}} \quad (1)$$

For each sample, at least three measurements were performed and the average values were

reported. The relative error for IEC measurements was less than 3%.

Degree of sulfonation of SPEEK polymer

The DS can be controlled by reaction time and temperature. The sulfonation degree is defined as the ratio of the molar number of sulfonated PEEK units to that of the total molar number of initial repeat units of PEEK. The DS can be calculated by the following equations.

$$\text{DS} = \frac{N_{\text{PEEK-SO}_3\text{H}}}{N_{\text{PEEK-SO}_3\text{H}} + N_{\text{PEEK}}} \quad (2)$$

Here, $N_{\text{PEEK-SO}_3\text{H}}$ and N_{PEEK} are the molar number of sulfonated PEEK units and molar number of unsulfonated PEEK units, respectively. According to the expression of DS, the molar number, $N_{\text{PEEK-SO}_3\text{H}}$ of the sulfonated PEEK unit in 1 g sulfonated PEEK polymer is:

$$N_{\text{PEEK-SO}_3\text{H}} = 0.001 \times \text{IEC} \quad (3)$$

The molar number of the PEEK unit in 1g sulfonated PEEK polymer is:

$$N_{\text{PEEK}} = \frac{1 - 0.001 \times \text{IEC} \times M_{\text{PEEK-SO}_3\text{H}}}{M_{\text{PEEK}}} \quad (4)$$

where, $M_{\text{PEEK-SO}_3\text{H}}$ and M_{PEEK} are the molecular weights of the PEEK-SO₃H unit and the PEEK unit respectively. $M_{\text{PEEK-SO}_3\text{H}} = 368$ Da and $M_{\text{PEEK}} = 288$ Da.

Water and methanol uptake

Membrane samples of area approximately 3 cm × 3 cm were dried at 100°C for 4 h to bring each sample to an identical starting state. The membrane samples were then weighed to note the dry weight (W_d). Then the dried membrane samples were immersed in deionized water for 48 h. After that, it was taken out and the surface-attached water of the membranes was removed with blotting paper, the membranes were immediately weighed and measured (W_s). The water uptake of the membrane was calculated according to the following equation.³⁴

$$\text{Water uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (5)$$

where, W_s and W_d are the weight of the wet membrane and dry membrane, respectively. Methanol uptake was also calculated in the same way using 1.0M methanol solution. For each sample, at least five measurements were performed and the average values were reported. The relative errors for water

uptake and methanol uptake measurements were about 5%.

Thermo-gravimetric analysis

The thermo-gravimetric analysis (TGA) for thermal stability was performed under nitrogen atmosphere on a TGA/SDTA851e/LF/1100 model (Mettler Toledo, Greifensee, Switzerland) instrument using a heating rate of 10 °C/min from 25°C to 900°C.

X-ray diffraction

X-ray diffraction (XRD) profile of membrane and ZTP powder was recorded under air at room temperature using AXS D8 ADVANCE Fully Automatic Powder X-Ray Diffractometer (Bruker, Greifensee, Switzerland). The patterns were acquired for 2θ range of 5–70° with a 0.05 degree s⁻¹ scan speed.

Fourier transforms infrared spectroscopic analysis

Fourier transforms infrared (FTIR) spectrum of the polymer and ZTP powder was recorded in the 4000–450 cm⁻¹ region using spectroscopic KBr powder with a Perkin-Elmer spectrometer (Spectrum one mode, Waltham, MA).

Scanning electron microscope

The morphology of the membrane and ZTP powder was observed using a LEO 1430VP scanning electron microscope (SEM).

Surface Area Measurement

The BET (Brunauer-Emmet-Teller) specific surface area and pore volume of the ZTP powder was determined by N₂ adsorption-desorption isotherm at 77 K measured in a surface area analyzer (make: Beckman-Coulter; model: SA 3100). Prior to the N₂ adsorption-desorption analysis, the sample was degassed at 120°C for 3 h. The surface area was calculated using multiple point BET model. The pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99 assuming all the pores are filled.

Proton conductivity

Proton conductivity (σ) of the membranes was measured at room temperature (25°C) by AC impedance technique over the frequency range between 10 kHz and 100 mHz using a potentiostat (Autolab, PGSTAT 302N). Before the measurement, the membrane was equilibrated with de-ionized water for at least 24 h.³⁵ Then the membrane was clamped between two compartments. One compartment was

filled with water and another compartment was filled with 0.25M H₂SO₄. Working electrode (Pt) and reference electrode were kept in H₂SO₄ compartment. Counter electrode (Pt) was kept in water compartment. The proton conductivity of membrane, σ (S cm⁻¹), was calculated according to eq. (6):

$$\sigma = \frac{L}{RS} \quad (6)$$

where, L , R , and S are the distance between the electrodes (cm), the measured resistance (ohm), and membrane area (cm²), respectively. Three measurements were performed for each membrane and the average values were reported.

Methanol permeability

Methanol permeability through the membrane was measured at room temperature (25°C) by potentiometric technique with a Potentiostat (Autolab, PGSTAT 302N) using the three electrode technique.³⁵ Methanol permeability was investigated in a two-compartment permeability cell. The membrane was clamped between two compartments. One compartment (A) was filled with 1M methanol in 0.5M H₂SO₄ solution while the other compartment (B) was filled with 0.5M H₂SO₄ solution only. Platinum (Pt) electrodes were used as counter and working electrodes and the Ag/AgCl was used as reference electrode. After methanol reaches the H₂SO₄ compartment (B), the Pt electrode senses the methanol and its potential tends to shift, which was recorded using Potentiostat (Autolab, PGSTAT 302N). Methanol concentrations were obtained using the potential vs. concentration calibration curve. To estimate the methanol permeability, methanol concentration in the compartment (B) containing only the H₂SO₄ was measured at regular time of intervals. The methanol permeability (P) was calculated using the following relationship:

$$C_B = \frac{AP}{V_B l} C_A t \quad (7)$$

where C_B is concentration of methanol in compartment B (M) at time t (s), C_A is the initial concentration of methanol in compartment A (M), A is membrane area (cm²), V_B is volume of compartment B (cm³), and l is thickness of membrane (cm).

RESULTS AND DISCUSSION

Sulfonation of PEEK

Sulfonic acid groups (-SO₃H) are functionalized onto the PEEK unit structure by a sulfonation reaction in order to obtain ionic conductivity. PEEK is a

TABLE I
Properties of SPEEK Polymer Synthesized at Different Reaction Time

Sample	Reaction time (h)	IEC (meq/g)	DS (%)	Water swelling
SPEEK-1	1	0.749	22.9	-ve
SPEEK-2	2	1.843	62.3	-ve
SPEEK-3	3	2.125	73.73	+ve

thermally stable polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (—O—) and carbonyl (—CO—) linkages.^{36,37} Sulfonation is an electrophilic substitution reaction that preferentially takes place in the high electron density site. Substitution occurs in one of the four positions of the aromatic ring between the ether bridges because the electron density of the other two aromatic rings in the repeat unit is relatively low due to the electron-attracting nature of the neighboring carboxyl group.^{8,34,38,39} It is known that the reaction time, acid concentration, and reaction temperature have effects on the DS of sulfonated polymers. With the concentrated sulfuric acid used in this work at 55°C, there is at most one —SO₃H group attached to each repeating unit.^{37–39}

Table I reports the properties of SPEEK polymers synthesized at different reaction duration. As can be seen that the IEC and DS values increase with duration of sulfonation reaction, which is good for DMFC application. Increasing the reaction duration allows more sulfonic acid group to attach to the PEEK polymer backbone having larger amount of potentially mobile cations. However, SPEEK-3 sample (3 h sulfonation reaction) indicates positive water swelling (highly soluble in water at room temperature) when compared with SPEEK-1 and SPEEK-2. Despite of higher IEC, SPEEK-3 sample is not useful

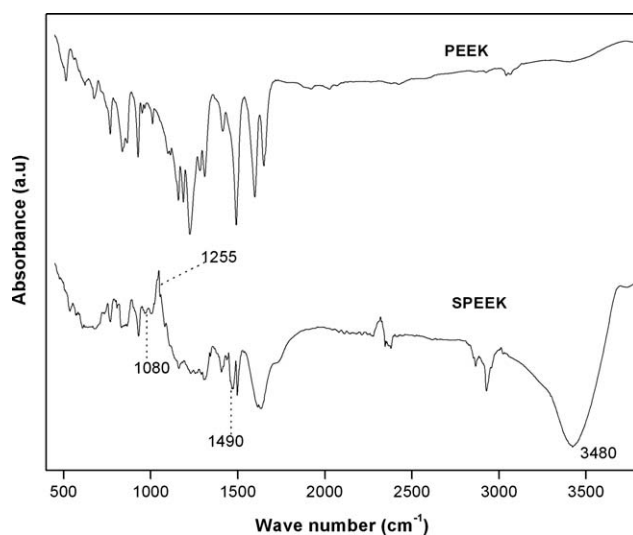


Figure 1 FTIR spectrum of PEEK and SPEEK polymer.

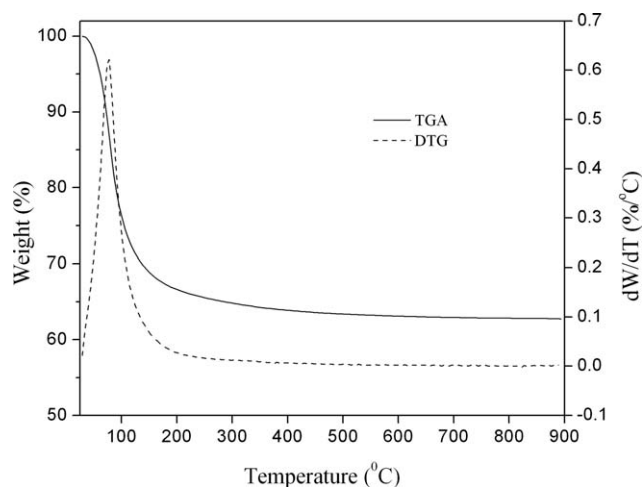


Figure 2 TGA and DTG curves of the ZTP powder.

for DMFC application. Therefore in this work, we have used SPEEK-2 sample for making composite membranes and pure SPEEK membrane based on its higher IEC and DS value compared to SPEEK-1.

To confirm the presence of sulfonic acid groups in the SPEEK polymer, we have carried out the FTIR spectrum of PEEK and SPEEK samples as shown in Figure 1. The broadband in SPEEK samples appearing at 3480 cm⁻¹ is assigned to O—H vibration from sulfonic acid groups interacting with molecular water.^{37,40} The aromatic C—C band at 1490 cm⁻¹ for PEEK was observed to split due to new substitution upon sulfonation.^{41,42} A new absorption band at 1080 cm⁻¹ which appeared upon sulfonation is assigned to sulfur-oxygen symmetric vibration O=S=O.^{8,40} The new absorptions at 1255, 1080, and 1020 cm⁻¹ which appeared in sulfonated samples are assigned to the sulfonic acid group in SPEEK.⁴³ All these results obtained from the comparison of characteristic absorption bands between PEEK and SPEEK confirm the sulfonic acid groups into the polymer chains.

Characterization of ZTP

Figure 2 shows the TGA and DTG analysis of ZTP. The TGA result of the ZTP sample shows a sharp change within the temperature range of 80–180°C corresponding to the loss of external water molecules, after which a gradual weight loss is observed.³⁰ This may be due to the condensation of structural hydroxyl groups. The total weight loss of ZTP is found to be around 36 wt % at 900°C. The endothermic peak observed around 100°C in the DTG plot also confirms the removal of external water molecules. FTIR spectrum of the ZTP sample is presented in Figure 3. It exhibits a broad band in the region of 3434 cm⁻¹, which is attributed to asymmetric and symmetric hydroxyl (OH) stretches. A

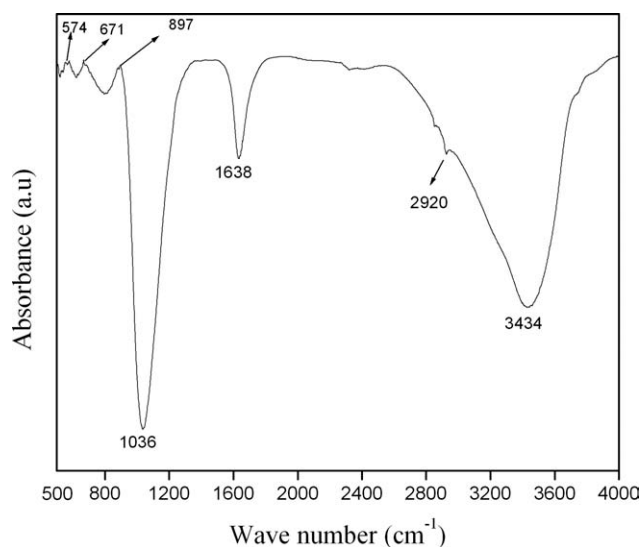


Figure 3 FTIR spectrum of the ZTP powder.

sharp medium band at 1638 cm^{-1} is attributed to aquo (H—O—H) bending. A band in the region $\sim 1036\text{ cm}^{-1}$ is attributed to Ti—O—P stretching.³⁰ The peak characteristic of Zr—O—Zr bonds appears around 671 cm^{-1} . The peak visible around 897 cm^{-1} is likely to be derived from Ti—O—Ti stretching. Figure 4 depicts the XRD pattern of the ZTP powder. The absence of sharp peaks in the XRD pattern indicates the amorphous nature of material. Figure 5 shows the SEM image and energy dispersive X-ray spectroscopy (EDX) analysis of the ZTP powder. The EDX analysis reveals the presence of Zr, Ti, P, and O. From the SEM image, it can be clearly seen the amorphous nature of the material. N_2 adsorption/desorption isotherm of the ZTP powder is shown in Figure 6. The isotherm corresponds to type IV, indicating typical mesoporous material. The specific surface area and pore volume of the ZTP powder are found to be $352\text{ m}^2\text{ g}^{-1}$ and $0.297\text{ cm}^3\text{ g}^{-1}$, respectively. The IEC of ZTP powder was determined according to the procedure reported elsewhere⁴⁴ and is found to be 3.01 meq/g .

Characterization of SPEEK composite membranes

Ion exchange capacity and degree of sulfonation

IEC is usually defined as the moles of fixed SO_3^- sites per gram of polymer. It plays a crucial role for the proton conductivity of the membranes in the fuel cell. The titrated IEC value confirms the content of fixed SO_3^- sites in the composite membranes. Figure 7 represents the influence of ZTP loading on the IEC of the composite membranes. The IEC value of SPEEK is found to be higher than that of the Nafion[®] 117 (0.91 meq/g) membrane.⁴⁵ Pure SPEEK membrane shows an IEC value of 1.45 (meq/g) and after incorporating ZTP into the polymer matrix, IEC

is increased up to 5% loading after that it starts decreasing, which may be due to the increased interaction between sulfonic acid groups of the polymer matrix and ZTP particles at higher loading. Similar trend was also reported by Jang et al.⁴⁶ for SPEEK/tungstophosphoric acid (TPA) composite membrane. The composite membrane with 5 wt % ZTP loading indicates IEC value of 1.72 meq/g and 15% ZTP loaded membrane shows a value of 1.33 meq/g . The water content strongly depends on the sulfonic acid content and is also related to the IEC. Therefore, proper water content should be maintained in sulfonated polymer membranes to guarantee high proton conductivity. The DS value of the pure SPEEK membrane (synthesized at 2-h reaction time) determined from IEC value is found to be 47%. The pure SPEEK membrane shows a lower value of DS (with IEC of 1.45 meq/g) compared to the corresponding SPEEK polymer (with IEC of 1.843 meq/g) (see Table I). This may be due to the interaction between SPEEK polymer and DMAc solvent. The major drawback of the SPEEK–DMAc interaction is the reduction of the number and/or mobility of protons available for proton transport and dramatically reduces the membrane conductivity.⁴¹

Water and methanol uptake

It has been widely reported in the literature that the proton conductivity of the sulfonated polymers is associated with the water uptake and IEC of the membranes. In general, proton conductivity depends on the number of available sulfonic acid groups and their dissociation capability in water. Water uptake is an important parameter in studying PEMs, because the water resides in the hydrophilic domains and can facilitate the transport of protons,

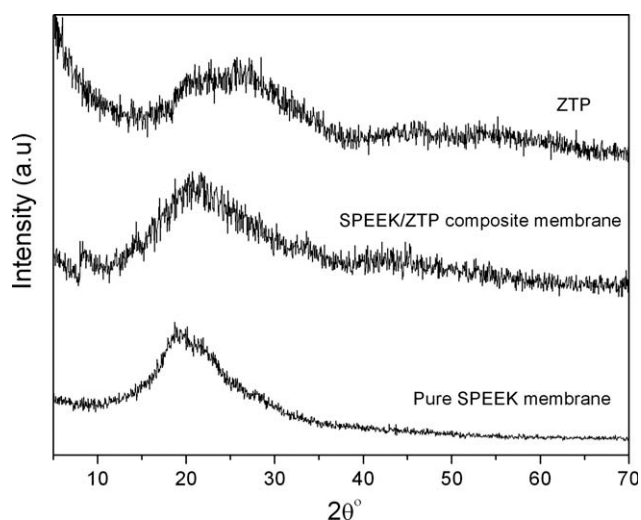


Figure 4 XRD patterns of the ZTP powder, pure SPEEK membrane, and SPEEK/ZTP composite membrane.

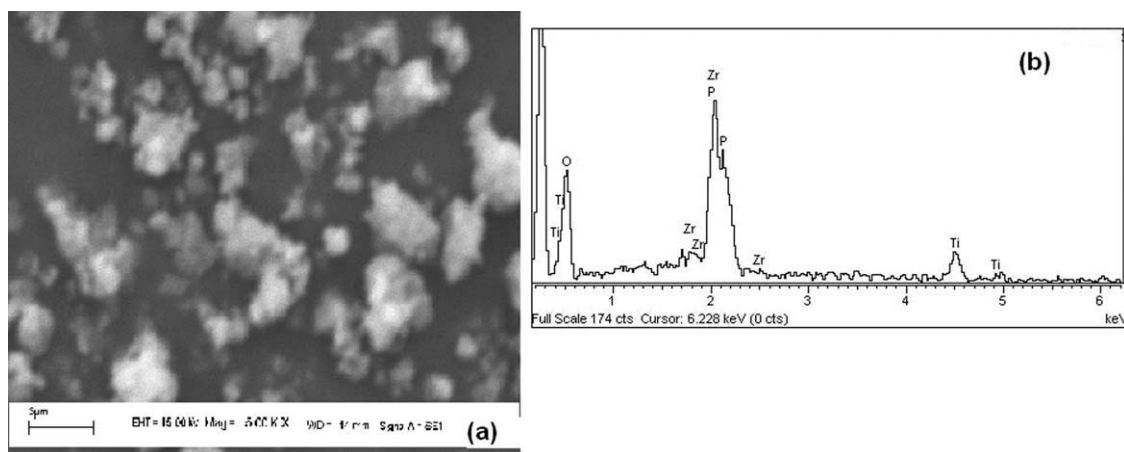


Figure 5 SEM (a) and EDX (b) analysis of the ZTP powder.

but large quantity of water absorption results in loss of mechanical stability.⁴⁷

Water uptake values decrease with an increase in weight fraction of ZTP in the membrane matrix as depicted in Figure 8. For example, the water uptake of pure SPEEK membrane is around 24.3%, whereas SPEEK/ZTP composite membranes show the water uptake of 22.2%, 17.5%, and 16.9%, respectively, for 5, 10, and 15 wt % ZTP loading. It is believed that the water uptake in polymers is increased due to the membrane swelling and resulting pore expansion, which is caused by interaction with a solvent. The SPEEK composite membranes exhibit lower water uptake when compared to pure SPEEK although the additives are hydrophilic in nature. The reason for the reduction in the water uptake of composite membranes is due to the incomplete removal of water from the membrane under the drying conditions applied. This is attributed to strong interactions

between the sulfonic acid group in the polymer and the ZTP additive. Water uptake value of Nafion 115 and Nafion 117 membrane was about 20% and 20.6%, respectively.^{9,45}

The variation of methanol uptake with ZTP loading is also shown in Figure 8. It is observed that the methanol uptake of the composite membrane also decreases with an increase in the ZTP loading. The methanol uptake of the composite membrane (with 15 wt % ZTP) is found to be 10.4%, which is twofold lower than that of the pure SPEEK membrane (23%). This may be due to the blocking of pores by ZTP particles. The methanol uptake of Nafion 117 membrane was about 35% in 1.0M methanol solution.

Thermal stability

It is essential for a polymer membrane to possess adequate thermal stability for DMFC application. Many researchers have already confirmed the high thermal stability of the SPEEK. However, the incorporation of inorganic materials into the SPEEK

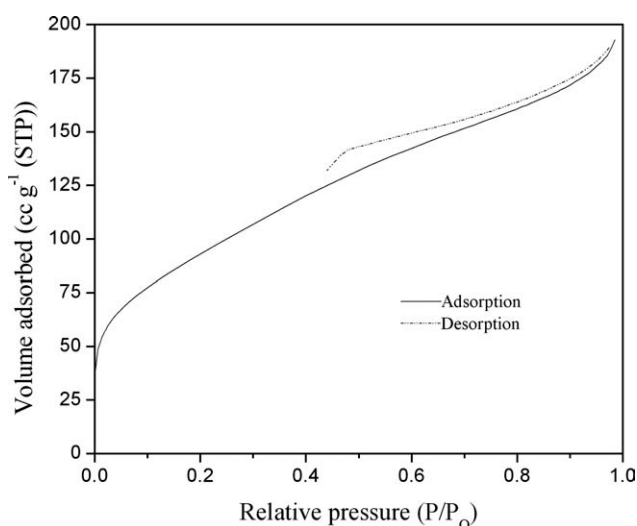


Figure 6 N₂ adsorption/desorption isotherm of ZTP powder.

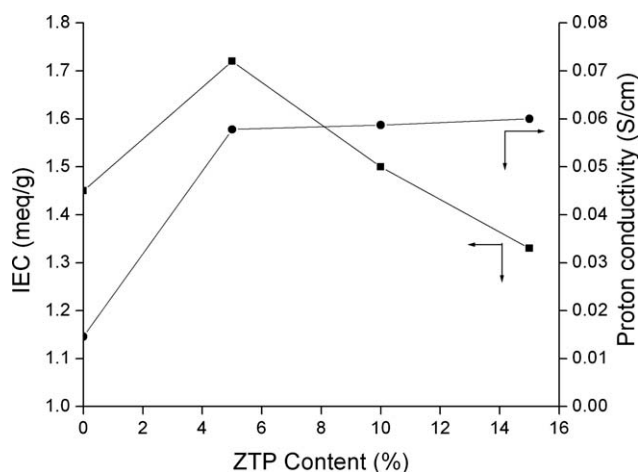


Figure 7 Variation of IEC and proton conductivity of the composite membranes with ZTP content.

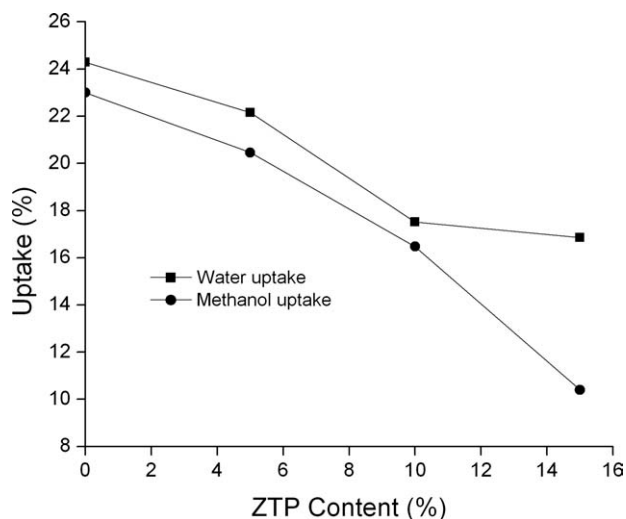


Figure 8 Variation of water uptake and methanol uptake (in 1M solution) of the composite membranes with ZTP content.

matrix may affect its thermal stability. To examine this property, TGA analysis was carried out from room temperature to 900°C at a heating rate of 10 °C/min under nitrogen atmosphere. The TGA curves for PEEK, SPEEK, and SPEEK/ZTP composite membranes are presented in Figure 9. The onset of weight loss for PEEK polymer takes place at about 520°C. This weight loss is due to the main chain decomposition, which results in the formation of phenols and benzene.³⁷ In the curves of SPEEK and SPEEK/ZTP composite membrane, three subsequent steps of weight loss are observed. The first weight loss corresponds to the physically adsorbed water in the polymer. The second weight loss is related to the decomposition of sulfonic acid groups from main chain of PEEK. Third weight loss (>409°C) is attributed to the degradation of main

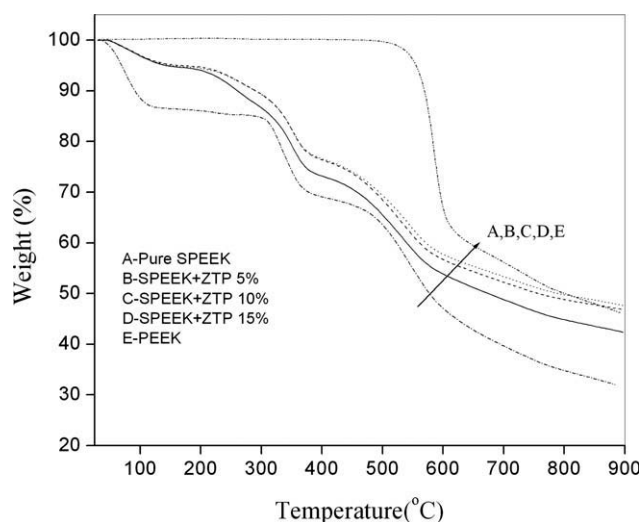


Figure 9 TGA of the SPEEK/ZTP composite membranes, pure SPEEK membrane, and PEEK polymer.

TABLE II
Thermal Properties of SPEEK/ZTP Membranes

Name of sample	T_{onset} (°C)	Temperature at 15% weight loss, T_{15} (°C)	Temperature at 50% weight loss, T_{50} (°C)	ΔT_{15} (°C)	ΔT_{50} (°C)
Pure SPEEK	279	297	570	–	–
SPEEK/ZTP5	294	311	700	14	130
SPEEK/ZTP10	284	334	796	37	226
SPEEK/ZTP15	290	335	798	38	228

chain of PEEK, which shifts to lower temperature from 520 to 409°C as compared to the neat PEEK.³⁴

Table II shows the onset of weight loss temperature, 15 and 50% weight loss temperature of pure SPEEK, and composite membranes. The degradation of sulfonic acid groups in SPEEK starts at 279°C. But in the case of composite membrane (5 wt % ZTP loading), thermal degradation begins at 294°C. When 15% weight is chosen as a point of comparison, the decomposition temperature are 297, 311, 334, and 335°C for pure SPEEK, composite membranes having 5, 10, and 15 wt % ZTP loading, respectively. These results indicate that the incorporation of ZTP shifts the decomposition temperature to higher direction and hence enhances the thermal stability by 14–38°C and 130–228°C, respectively, when 15 and 50% weight is chosen as a point of comparison. The temperature of onset weight loss is all above 279°C, which reveals the adequate thermal properties of composite membranes for usage as proton exchange materials in DMFC.

From the results of differential thermo gravimetric (DTG) analysis of SPEEK and composite membranes (see Fig. 10), three endothermic peaks are clearly observed. In the case of SPEEK membrane, the first

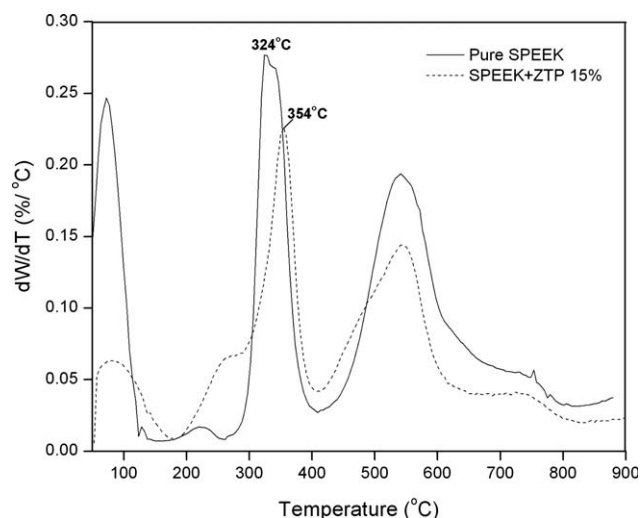


Figure 10 DTG curve of pure SPEEK membrane and SPEEK/ZTP composite membrane.

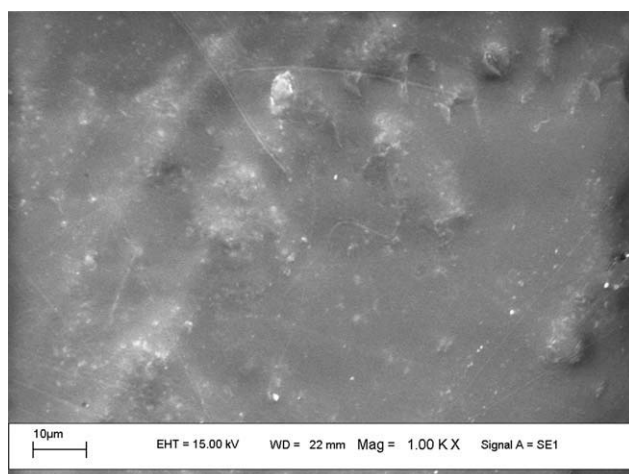


Figure 11 SEM micrograph of the surface of the SPEEK/ZTP composite membrane.

peak around 90°C corresponds to the removal of adsorbed water molecules. The second peak at 324°C is ascribed to sulfonic groups degradation. Third peak at 541°C corresponds to the degradation of main chain of PEEK. For composite membranes, the second endothermic peak corresponding to sulfonic groups degradation is observed at higher temperature (354°C) compared to pure SPEEK membrane (324°C). It also further confirms the enhancement of thermal stability of the composite membrane over pure SPEEK membrane.

XRD and SEM analysis

Figure 4 shows the XRD of pure SPEEK membrane and SPEEK/ZTP composite membrane. The XRD pattern of SPEEK is diffuse, which indicates the absence of the crystalline phase. In the diagram of SPEEK composite membrane, the ZTP peaks are overlaid by the broad SPEEK reflection. It is clear from Figure 4 that all the membranes are amorphous in nature. It is to be noted that the incorporation of ZTP into the SPEEK has not disturbed the amorphous nature of the membrane. The morphology of the composite membrane was studied by SEM. SEM micrograph of surface of the SPEEK composite membrane is presented in Figure 11. It shows that the solid ZTP particle is well mixed with SPEEK and the particles are randomly distributed.

Proton conductivity

Figure 7 shows the variation of proton conductivity at room temperature with ZTP loading in the membrane. In general, as the water uptake decreases proton conductivity will also decrease. However in our work, the proton conductivity increases when the water uptake decreases. The enhancement in

conductivity upon addition of ZTP can be rationalized using prior reports in the literature.^{48–50} This phenomenon has been observed by Kim et al.⁴⁹ in composite PEMs based on heteropolyacid in sulfonated polysulfones.

The presence of the additive was found to enhance the proton conductivity, while at the same time decreasing the water uptake.^{48,49} They have interpreted the lower water uptake as being due to incomplete removal of water from the membrane under the drying conditions applied. This is attributed to strong interactions between the sulfonic acid group in the polymer and the additive.⁵¹ The enhanced proton conductivity is attributed to the retention of water. Similarly, Karthikeyan et al.⁵⁰ reported increasing proton conductivity, but lower water permeation upon addition silica to SPEEK (until a loading of 10 wt % is reached). They too attribute the higher proton conductivity of the composite membranes to the enhanced ability of the additive particles to retain water. The conductivity results obtained in this study are very similar to those reported in the above studies and it is likely that a similar mechanism is in place. For comparison, the proton conductivity of Nafion117 membrane was also measured under the same conditions and was found to be $2.58 \times 10^{-2} \text{ S cm}^{-1}$. The obtained result is comparable with the results reported in the literature (0.023 S cm^{-1}).⁵² This result clearly demonstrates that the proton conductivity of the composite membrane with 15% ZTP content at room temperature (0.06 S cm^{-1}) is about twofold higher than the commercial Nafion membrane.

Methanol permeability

Figure 12 explains the variation of methanol permeability of the SPEEK composite membranes at room

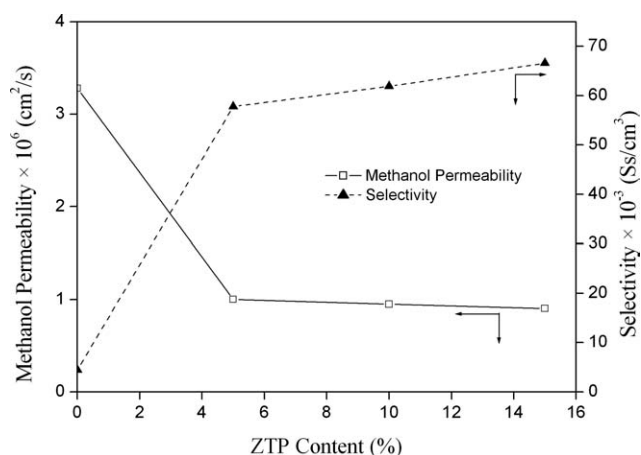


Figure 12 Variation of methanol permeability and selectivity of the SPEEK composite membranes with ZTP content.

temperature with ZTP loading. All the composite membranes have higher potential values compared to the pure SPEEK membrane. These potential values were recorded and converted to concentrations using the calibration curve. The concentration values were used in determining the methanol permeability of the membranes. The methanol permeability of the composite membranes decreases with an increase in the ZTP loading (methanol permeability value of pure SPEEK and SPEEK/ZTP (15 wt %) composite membrane is 3.28×10^{-6} , $0.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively). The incorporated ZTP particles block the channels to methanol passing as was confirmed previously by methanol uptake measurements (see Fig. 8). This may be the reason for the reduction of methanol permeability after incorporating ZTP. The methanol permeability value of the commercial Nafion 117 at room temperature was reported as $1.09 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.⁵²

Overall membrane performance

The performance of the membranes strongly depends on proton conductivity and methanol permeability. An ideal electrolyte membrane must have the highest proton conductivity and the lowest methanol permeability to exhibit optimum properties. However, most of the studies have shown simultaneous increase or decrease in the proton conductivity and methanol permeability. The selectivity (Φ) is defined as follows:

$$\Phi = \frac{\sigma}{P} \quad (8)$$

where σ and P are the proton conductivity and methanol permeability of membrane, respectively.⁵³ The selectivity of the composite membranes with different ZTP loading is shown in Figure 12. The selectivity of the composite membranes enhances when the ZTP loading increases from 0 to 15 wt %. The maximum selectivity value of $6.66 \times 10^4 \text{ Ss cm}^{-3}$ is observed for the composite membrane with 15% ZTP loading (SPEEK/ZTP15). The selectivity of the commercial Nafion 117 membrane at room temperature was found to be $2.37 \times 10^4 \text{ Ss cm}^{-3}$.

To show that the prepared SPEEK/ZTP composite membranes have greater advantage over the synthesized pure SPEEK membrane and the commercial Nafion 117 membrane, we have calculated the percent improvement in the proton conductivity, selectivity, and percent decrement of methanol permeability. As the ZTP loading increases from 5 to 15%, the proton conductivity of the composite membranes shows an improvement from 296% to 311% whereas the methanol permeability confirms a decrement from 228% to 264% when compared with pure

SPEEK membrane. Since the selectivity depends on proton conductivity and methanol permeability values, it also shows an increment of 1199–1397%. It is clearly seen that when compared with the commercial Nafion 117 membrane, the proton conductivity of the composite membranes shows an improvement from 124 to 133% whereas the methanol permeability illustrates a decrement from 9 to 21% as the ZTP loading raises from 5 to 15%. Over all, the selectivity of the SPEEK/ZTP composite membrane is found to be about fifteen, threefold higher than the pure SPEEK membrane and the commercial Nafion 117 membrane, respectively. From this comparison study, it can be concluded that the SPEEK composite membranes prepared with different ZTP loading is better than that of the pure SPEEK membrane and commercial Nafion membrane.

Membrane cost

A thorough analysis of membrane cost has been made by Gebert et al.⁵⁴ comparing the cost of Nafion, sulfonated PEEK, and other non-fluorinated membranes. Materials costs and production costs were taken into account. Non-fluorinated alternatives such as SPEEK could be cheaper as inexpensive raw material can be used. In the case of SPEEK, the production process is simpler and total processing time comparable to that of Nafion. Moreover, advantageous points in the synthesis of SPEEK over Nafion are the low number of operation units and the absence of gaseous reactants, which lead to high-space time yields, especially at viable residence times of some 15 h. The production of SPEEK entails about 40% less investments in comparison to the fluorinated polymers.³⁷ The cost of fluorinated membranes such as Nafion (Du Pont) and Dow membranes (Dow Chemicals Co.) is reported as US\$ 800–2000 m^{-2} .³⁷ The cost of fabricated SPEEK composite membranes is estimated based on the raw materials and fabrication cost. The projected cost of SPEEK composite membranes is found to be US\$ 323 m^{-2} (approximate). The reported value of the membrane cost may vary significantly depending on the raw materials and fabrication cost. It is a confirmation that as long as fluorinated materials (Nafion) are used, a strong cost reduction might be hard to achieve. The result of cost estimation indicates that the fabricated SPEEK composite membranes are of low cost than that of the commercial Nafion membranes based on the raw materials and fabrication cost. Hence it can be utilized as low cost alternative for the high cost Nafion for DMFC application.

CONCLUSIONS

SPEEK polymers with different DS have been successfully prepared using concentrated H_2SO_4 as a

sulfonating agent at 55°C by varying the reaction time. The SPEEK polymer prepared with 3-h reaction (SPEEK-3) showed higher DS and IEC, however it swells more in water. From the results of DS and swelling behavior of the SPEEK polymer samples, SPEEK-2 sample is selected for the preparation of the SPEEK composite membranes with different loading of ZTP. The increase in ZTP loading in the composite membrane decreases the water uptake and methanol uptake. Thermal stability of the membrane is enhanced after incorporating the ZTP as compared with pure SPEEK membrane. The degradation of the SPEEK composite membranes are well above the normal operating temperature of DMFC. The proton conductivity of composite membrane is about fourfold higher than the pure SPEEK membrane and increases with increase in ZTP loading. The methanol permeability of composite membranes is decreased about 264%, 21% as compared to pure SPEEK membrane, and Nafion 117 membrane, respectively. Permeation of methanol through the composite membrane decreases as the ZTP loading increases from 0 to 15%. Over all, the performance (selectivity) of the composite membranes increases with an increase in ZTP loading and is better than the commercial Nafion membrane and pure SPEEK membranes. Hence, the inexpensive SPEEK composite membrane could be used as an alternative for the high cost Nafion membranes.

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