ORIGINAL ARTICLE

High-performance SPEEK/SWCNT/fly ash polymer electrolyte nanocomposite membranes for fuel cell applications

Gandhimathi Sivasubramanian[1], Krishnan Hariharasubramanian[1], Paradesi Deivanayagam[2] and Jeyalakshmi Ramaswamy[2]

Sulfonated poly (ether ether ketone) (SPEEK)-based polymer nanocomposite membranes containing single-walled carbon nanotubes (SWCNTs) and fly ash as inorganic fillers have been prepared using a solution casting technique. The degree of sulfonation of poly (ether ether ketone) was determined by proton nuclear magnetic resonance spectroscopy analysis and was found to be 64%. Scanning electron microscopy and X-ray diffraction analyses confirmed the incorporation of nanofillers into the polymer matrix. The physicochemical properties of the prepared membranes were studied to evaluate their suitability for fuel cell applications. The SP-CNT-FA-8 membrane exhibited the highest proton conductivity of 0.027 S cm^{-1} at 30 °C and 0.034 S cm^{-1} at 90 °C, whereas the pristine membrane exhibited conductivities of 0.019 S cm^{-1} at 30 °C and 0.031 S cm^{-1} at 90 °C. The membrane electrode assemblies were successfully fabricated for the pristine SPEEK and SP-CNT-FA-6 membranes, and their electrochemical performance was studied throughout the current density range. In addition to the favorable proton conductivity, the electrolyte membranes showed excellent thermal and mechanical stability; taken together, these results indicate that the composite membranes based on SPEEK with SWCNT and fly ash can be viable candidates for use as an electrolyte membrane in fuel cell applications.

INTRODUCTION

Fuel cells have been receiving increasing attention because of their application in stationary and mobile electronic devices and their automotive applications. Their high energy density, fewer corrosion issues and lower operating temperature make fuel cells promising candidates for various applications.[1] The proton exchange membrane is a key component in the fuel cell system and functions as an electrolyte to transfer protons from the anode to the cathode. The membrane acts as a barrier to the passage of electrons between the electrodes. Breakthroughs in the further development of fuel cell technology are inhibited by the lack of proton conducting membranes. Perfluoro sulfonic acid ionomers such as Nafion, Aciplex and Flemion are state-of-the-art materials found in fuel cell applications.[2] Although fluorinated polymers have several advantages,[3,4] they also exhibit a variety of problems, such as complicated synthesis, high cost, fuel crossover and reduced proton conductivity at elevated temperatures. To overcome these difficulties, there is a need to develop alternative polymer electrolyte membrane materials.

Poly (ether ether ketone) (PEEK) is a high-performance material that has good chemical resistance and excellent thermal and mechanical stability. The aromatic backbone of the PEEK helps to maintain the thermal and mechanical strength and allows chemical modification in polymer electrolyte membranes.[5,6] Introducing sulfonic acid functionality to the polymer backbone increases the hydrophilicity, resulting in an increase in proton conductivity.[7] The sulfonated form of PEEK has a low cost and is a good alternative to Nafion. Incorporating inorganic nanoparticles into a polymer matrix may improve its mechanical strength and durability.[8,9] Thus, the development and fabrication of organic–inorganic composite membranes using aromatic polymers is an alternative approach for obtaining membranes with good proton conductivity.[10–13] Modified PEEK-based membranes containing various fillers such as SiO_2,[14] TiO_2,[15] ZrO_2,[14,16] β-zeolite,[17] montmorillonite clay,[18] heteropolyacids such as phosphotungstic acid[19,20] and silicotungstic acid[21,22] have been widely studied.

A potential method for decreasing the polymer electrolyte membrane cost is to reduce its membrane thickness, which decreases the membrane resistance and thereby improves the fuel cell performance.[23,24] However, the thickness reduction leads to increased hydrogen and methanol permeability. Thus, the proton conductivity and water uptake ability of the membrane can be increased by introducing hygroscopic inorganic and organic additives, which keeps the membrane humid at higher temperatures while in operation.

[1]Department of Physics, Valliammai Engineering College, Kattankulathur, Tamilnadu, India and [2]Department of Chemistry, SRM University, Kattankulathur, Tamilnadu, India
Correspondence: Professor K Hariharasubramanian, Department of Physics, Valliammai Engineering College, Kattankulathur, Tamilnadu 603203, India.
E-mail: krishveni63@gmail.com
or Dr P Deivanayagam, Department of Chemistry, SRM University, Kattankulathur, Tamilnadu 603203, India.
E-mail: paradesi77@yahoo.com

Organic–inorganic composites are much more attractive electrolyte membranes in fuel cell applications.[25] Owing to the excellent mechanical, thermal, physical and electrical properties of carbon nanotubes (CNTs), many researchers have focused on the synthesis of advanced nanocomposites by using CNT as a filler to improve the performance and durability.[26–30] There is an emerging trend towards the development of composites via commercial and ecofriendly materials. The contribution of the inorganic oxides that are present in fly ash and CNTs enhances the performance of electrolytes in fuel cells. Fly ash is a by-product obtained from coal-fired power plants. The chemical composition of fly ash can vary considerably, but all variations of fly ash include oxides of silicon, aluminum, iron and calcium. Class F fly ash is a kind of melted glass and contains low-calcium fly ashes with a carbon content that is generally < 5.0% but can reach 10.0%. In recent years, fly ash has been identified as a cost-effective filler and has found potential applications in several fields.[31] Fly ash has been used as an efficient reinforcing agent in various polymers such as PEEK,[32] polyvinyl alchohol[33] and epoxy resin[34] in a variety of applications.

EXPERIMENTAL PROCEDURES

Materials
PEEK (GATONE 1100) powder was provided by Gharda Chemicals (Mumbai, India). Single-wall carbon nanotubes (SWCNTs) with 2–10 nm diameter and 1–5 μm length was purchased from Aldrich (St Louis, MO, USA). Class F fly ash was received from Thermal Power Plant (Gummidipoondi, Tamilnadu, India), and its chemical composition is given in Table 1. *N,N*-Dimethylacetamide (DMAC) was purchased from Merck (Mumbai, India).

Synthesis of sulfonated PEEK
The sulfonation of PEEK enhances both its hydrophilicity and the solubility of the polymer membranes.[35,36] The synthesis of sulfonated poly (ether ether ketone) (SPEEK) was performed according to the reported literature.[37,38] The powdered form of PEEK was first dried in a vacuum oven at 100 °C overnight. The sulfonation reaction was carried out using 125 ml of conc. sulfuric acid in a round bottom flask. A quantity of 2.5 g of dried PEEK powder was added slowly to the acid at ~ 40 °C over a period of 1 h. The reaction mixture was stirred constantly, and the temperature was maintained at 50 °C for 5 h. The viscous polymer solution was slowly poured into a large excess of ice water. The obtained product was filtered and washed repeatedly with distilled water until a neutral pH was reached. The resultant SPEEK was dried at 100 °C in a vacuum oven for 18 h.

Preparation of SPEEK/SWCNT/fly ash nanocomposites
The polymer nanocomposites were prepared by solution casting. The dried SPEEK polymer was dissolved in *N,N*-dimethylacetamide (5 wt%) and stirred at 40 °C for 15 min with constant speed using magnetic stirrer. The desired composition of SWCNT and fly ash with 2–8 wt% was added to the viscous solution under vigorous stirring. The temperature of the reaction mixture was slowly increased to 80 °C and maintained for 1 h. The resultant viscous polymer was casted on a flat glass plate and placed in a closed chamber for 24 h

Table 1 Chemical composition of fly ash

S. no	Name of the component	Weight (%)
1	SiO_2	47.55
2	Al_2O_3	33.45
3	CaO	2.099
4	Fe_2O_3	10.17
5	K_2O	1.65
6	MgO	0.005
7	Na_2O	0.015

to remove the solvent gradually. Subsequently, the membranes on the glass plates were dried at 60 °C for 6 h, 90 °C for 10 h and 120 °C for 6 h in a hot air oven. The glass substrates were soaked in deionized water overnight to release the membranes from the glass plates. The prepared polymer nanocomposite membranes were thoroughly washed with deionized water and dried at 100 °C under vacuum for 12 h. Figure 1 shows the process of preparing polymer nanocomposites. The thickness of the membranes was found to be between 30 and 36 μm, as presented in Table 2.

Measurements
PEEK sulfonation was confirmed by Fourier transform infrared spectroscopy. Small pieces of dried samples were scanned and recorded at a resolution of 4 cm^{-1} and at 21 scans per min in the region between 4000 and 500 cm^{-1}. The proton nuclear magnetic resonance (NMR) spectrum was recorded using an ASCEND-500 Instrument (Bruker, Billerica, MA, USA). The sample solution was prepared by dissolving the SPEEK polymer in deuterated dimethyl sulfoxide. The dispersion of CNT and fly ash in membranes was detected by X-ray diffraction (XRD) analysis using an XRD-Expert Hiscore Plus Instrument (PANalytical, Almelo, The Netherlands). The surface morphology of the polymer nanocomposites was investigated by scanning electron microscopy (SEM) using a GEG-200 (FEI Company, Eindhoven, The Netherlands). The dry membrane sample was kept under liquid nitrogen for 10 min. Before observation under the SEM column, the fresh membrane was vacuum sputtered with a thin layer of gold using an ion sputtering instrument.

The polymer membranes were dried in a vacuum oven at 100 °C until constant weights were attained. The measured weights and lengths of the respective membranes were noted as W_{dry} and L_{dry}. The dried membranes were then soaked in deionized water. The water on the membrane surface was swabbed using tissue paper, and its weight and length were measured and recorded as W_{wet} and L_{wet}. The water uptake and swelling ratio were calculated using Equations (1) and (2), respectively.

$$\text{Water uptake } \% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

$$\text{Swelling ratio} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \tag{2}$$

Ion-exchange capacity (IEC) is defined as the milliequivalent of H^+ per weight of the dry polymer. The IEC was measured using the back-titration method, as described in the literature.[39] The prepared SPEEK and nanocomposite membranes were stored in 1.0 M HCl for 24 h to bring the sample into complete SPEEK-H^+ form. The membranes were then rinsed with deionized water and equilibrated in 1.0 M NaCl solutions for 24 h to completely exchange the cations and obtain the SPEEK-Na^+ form. The NaCl solution was back-titrated with 0.1 M NaOH using the phenolphthalein indicator to determine the cations exchanged. The IEC of the electrolyte membrane was calculated using Equation (3)

$$\text{IEC}(\text{meq.g}^{-1}) = \frac{\text{Titre value} \times \text{Normality of NaOH}}{\text{weight of polymer}} \tag{3}$$

The thermal stability of the membrane was determined by thermogravimetric analysis (Q50; TA Instruments, New Castle, DE, USA). The weight loss of the polymers with increasing temperature was recorded at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The thickness of the membrane was measured by using a dial thickness gauge (Mitutoyo America Corporation, Aurora, IL, USA). The proton conductivity of the membranes was measured using an AC Impedance Spectrometer (Metrohm, KM Utrecht, Netherlands). Fully hydrated samples were sandwiched between two platinum plate electrodes of the same size. The conductivity (σ) of the composite membrane was calculated by measuring the resistance of the membrane. The relationship between the conductivity and resistance is given by Equation (4)

$$\sigma(\text{S.cm}^{-1}) = \frac{L}{RA} \tag{4}$$

where L is the thickness of the membrane, A is the area of the membrane under investigation and R is the resistance of the membrane. The tensile strength of the membranes was analyzed using a Universal Tester (Instron, Norwood, MA,
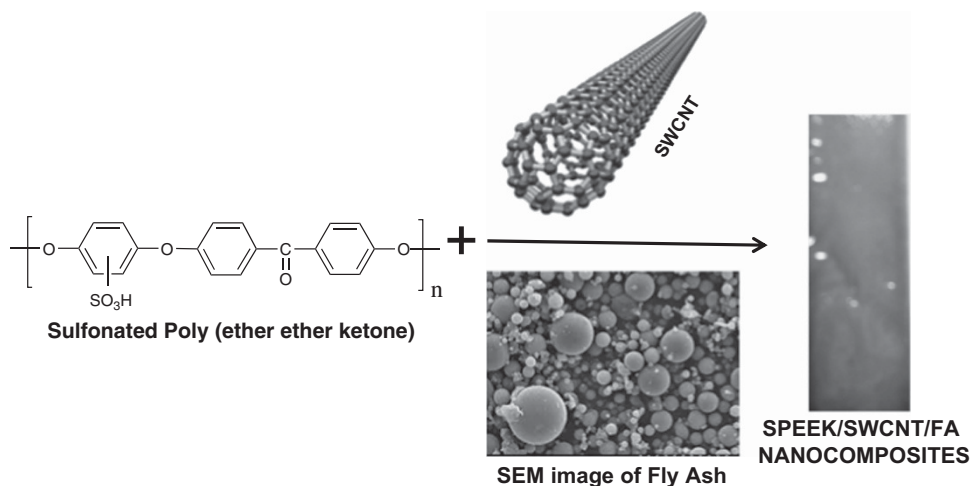
Figure 1 Illustrative representation of polymer nanocomposites. A full color version of this figure is available at the *Polymer Journal* journal online.

Table 2 Physicochemical properties of SPEEK and polymer nanocomposites

| Polymer code | Composition[a] (g) | | | Thickness (μm) | IEC (meq g^{-1}) | Water uptake (%) | Swelling ratio (%) | Tensile strength (MPa) |
	SPEEK	CNT	Fly ash					
SPEEK	1.00	0	0	36	1.86	23.1	7.8	54.6
SP-CNT-FA-2	0.96	0.02	0.02	32	1.80	23.8	7.2	58.1
SP-CNT-FA-4	0.92	0.04	0.04	33	1.73	24.4	6.9	63.3
SP-CNT-FA-6	0.88	0.06	0.06	32	1.68	25.8	6.6	68.0
SP-CNT-FA-8	0.84	0.08	0.08	30	1.59	27.3	6.0	74.4

Abbreviations: CNT, carbon nanotube; , *N,N*-dimethylacetamide; IEC, ion-exchange capacity; SPEEK, sulfonated poly (ether ether ketone); SWCNT, single-walled carbon nanotube.
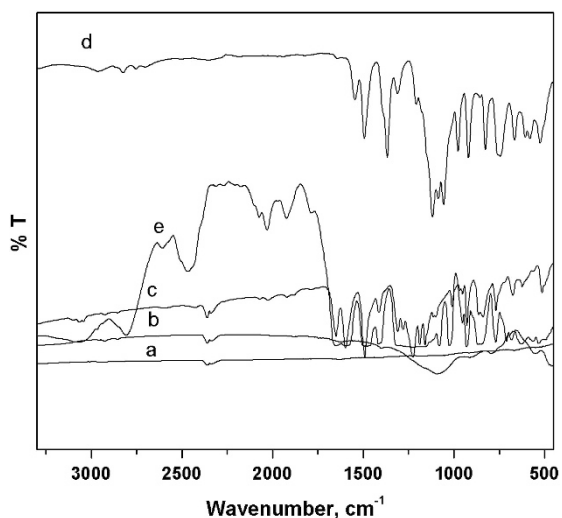[a]The concentration of SPEEK, SWCNT and fly ash in 20 ml of DMAC.

Figure 2 Fourier transform infrared (FT-IR) spectra of (**a**) Fly ash, (**b**) single-walled carbon nanotube (SWCNT), (**c**) poly (ether ether ketone) (PEEK), (**d**) sulfonated poly (ether ether ketone) (SPEEK) and (**e**) SP-CNT-FA-6.

USA). The samples were cut into pieces with a length of 50 mm and width of 20 mm and were tested using a 250 N load cell that was pulled at a rate of 50 mm min^{-1} within a 21-cm gauge length. Membrane electrode assemblies (MEAs) were fabricated by sandwiching the membrane between two electrodes, followed by hot pressing at 130 °C for 3 min. The cell potential of the membrane electrode assemblies with varying current densities was analyzed galvanostatically using a fuel cell test station (Bitrode Instruments, St Louis, MO, USA). The detailed technique of the measurement is reported in our earlier paper.[40]

RESULTS AND DISCUSSION

Spectral analysis

The PEEK sulfonation process was confirmed by Fourier transform infrared, as shown in Figure 2. The splitting of the aromatic C-C absorption band at 1495 cm^{-1} confirms the sulfonation reaction.[39] The symmetric stretching vibration of O=S=O was observed at ~1082 cm^{-1}, and the S=O vibration peak was observed at ~1027 cm^{-1}. Characteristic carbonyl stretching of the polymer was obtained at 1647 cm^{-1}. The sulfonation of PEEK was also confirmed by ^{1}H-NMR analysis, and the spectrum is shown in Figure 3. Zing *et al*.[41] reported on the reaction kinetics of PEEK sulfonation as studied by NMR spectroscopy.[41] The determination of the sulfonic acid group present in the SPEEK is based on the intensity signal observed at 7.52 p.p.m. in the NMR spectrum, as shown in Figure 3. The degree of sulfonation was calculated by the reported procedure[42] and was found to be 64%.

X-ray diffraction

The powder XRD patterns of the pristine SPEEK and nanocomposite membranes are shown in Figure 4. The broad band at 2θ indicates the amorphous nature of the polymer because of the presence of the hydrophilic sulfonic acid group. Generally, a more amorphous nature is expected to lead to higher water uptake and thus a higher proton conductivity.[43] Higher crystallinity generally prevents water from
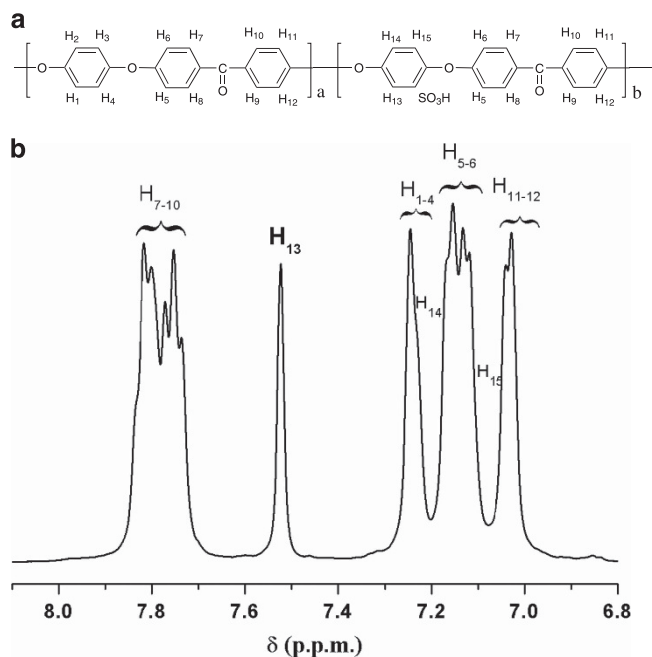
Figure 3 Nomenclature of (**a**) sulfonated poly (ether ether ketone) (SPEEK) repeat unit and (**b**) proton nuclear magnetic resonance (NMR) spectrum of SPEEK.

Figure 4 The X-ray diffraction (XRD) pattern of (**a**) single-walled carbon nanotube (SWCNT), (**b**) fly ash, (**c**) sulfonated poly (ether ether ketone) (SPEEK), (**d**) SP-CNT-FA-2 and (**e**) SP-CNT-FA-6.

entering the polymeric membrane. A broad peak appearing at 22° in the XRD pattern of SPEEK indicates a mixture of amorphous and crystalline components. The absence of crystalline peaks in the XRD results suggest the good dispersion of CNT and fly ash in the polymer matrix.

SEM analysis
The surface morphology of the polymers was investigated by field emission SEM (FE-SEM) analysis. The images of pristine SPEEK, SP-CNT-FA-2, SP-CNT-FA-4 and SP-CNT-FA-6 membranes are shown in Figure 5. Owing to the introduction of nanofillers, the SEM images of polymer nanocomposites clearly showed that more small pores are distributed on the surface of the polymeric membranes than on the pure membrane. Hence, the nanocomposite membranes can retain water molecules, thereby increasing the proton conductivity.

Water uptake and swelling ratio
Water uptake ability is an important parameter for sulfonated polymer membranes used in fuel cells. The sulfonic acid groups form hydrogen bonding interactions with water molecules, leading to increased water uptake. Hence, the water uptake depends directly on the amount of sulfonic acid groups present in the polymer backbone.[21] However, a higher water uptake often results in the swelling behavior of the electrolyte membranes, which reduces their mechanical stability. Hence, a balanced water retention with moderate swelling is required for the long-term operation of the membranes in fuel cell applications.

Figure 6 displays the % water uptake and the swelling ratio of the SPEEK and polymer nanocomposite membranes measured at 30 °C. It can be observed from the results that incorporating CNTs and fly ash into the SPEEK matrix slightly increase the water uptake while reducing the swelling behavior of the composites. This increase in the water uptake may be due to the hydrophilicity of the silica present in the fly ash. Further, the possible water channels formed by the hydrophilic intera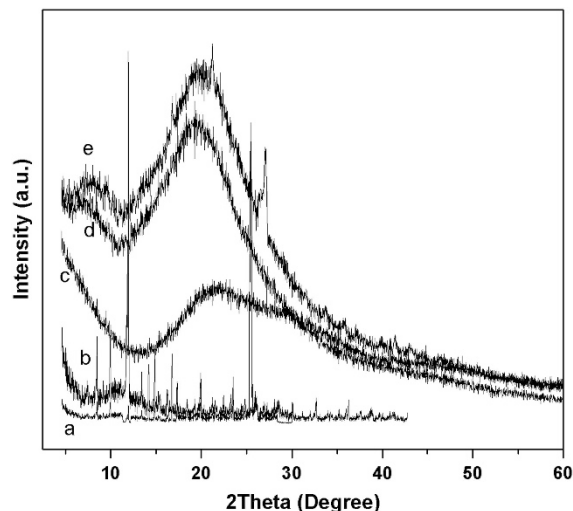ctions between SPEEK and fly ash may contribute to the water uptake. Owing to the good dimensional stability, the swelling ratio of the polymer nanocomposite was lower than that of the SPEEK, even though it exhibits higher water uptake values.

Ion-exchange capacity
IEC is generally defined as a measure of the number of exchangeable counter ions present in the polymer. It therefore provides information regarding the ionizable functional groups that exist in the polymer backbone and are responsible for membrane proton conduction.[44,45] The measured IEC values of pristine and polymer nanocomposites are shown in Table 2. The incorporation of SWCNT and fly ash into the polymer matrix led to a decrease in the IEC from 1.86 to 1.59 meq g^{-1}. This result indicates that the IEC of the polymer depends directly on the amount of sulfonic acid groups substituted in the polymer matrix.

Thermogravimetric analysis
The thermal stability of the PEEK, SPEEK and polymer nano-composites was measured by thermogravimetric analysis, and the thermograms are shown in Figure 7. All samples except PEEK showed three-step degradation patterns. In SPEEK and polymer nanocomposites, the first weight loss was observed because of the loss of absorbed moisture by the hygroscopic segment. The second step of degradation was observed ~300 °C, corresponding to the degradation of the aromatic sulfonyl groups. The final step indicates the decomposition of the aromatic polymer backbones. PEEK shows excellent thermal stability up to 750 °C. This indicates that the SPEEK-based polymer electrolyte materials are suitable for high-temperature applications. It is noted that incorporating inorganic fillers into the polymer matrix retards the oxidative degradation of SPEEK, leading to an improvement of the thermal stability of the electrolyte membranes.[6]

Mechanical stability
Good mechanical stability will enhance the durability of the membranes in fuel cell applications. Several approaches were adopted to increase the mechanical stability of the hydrophilic sulfonated polymers without compromising their proton conductivity.[46] To improve the mechanical stability, the tensile strengths of SPEEK and their nanocomposites were evaluated by a universal testing machine
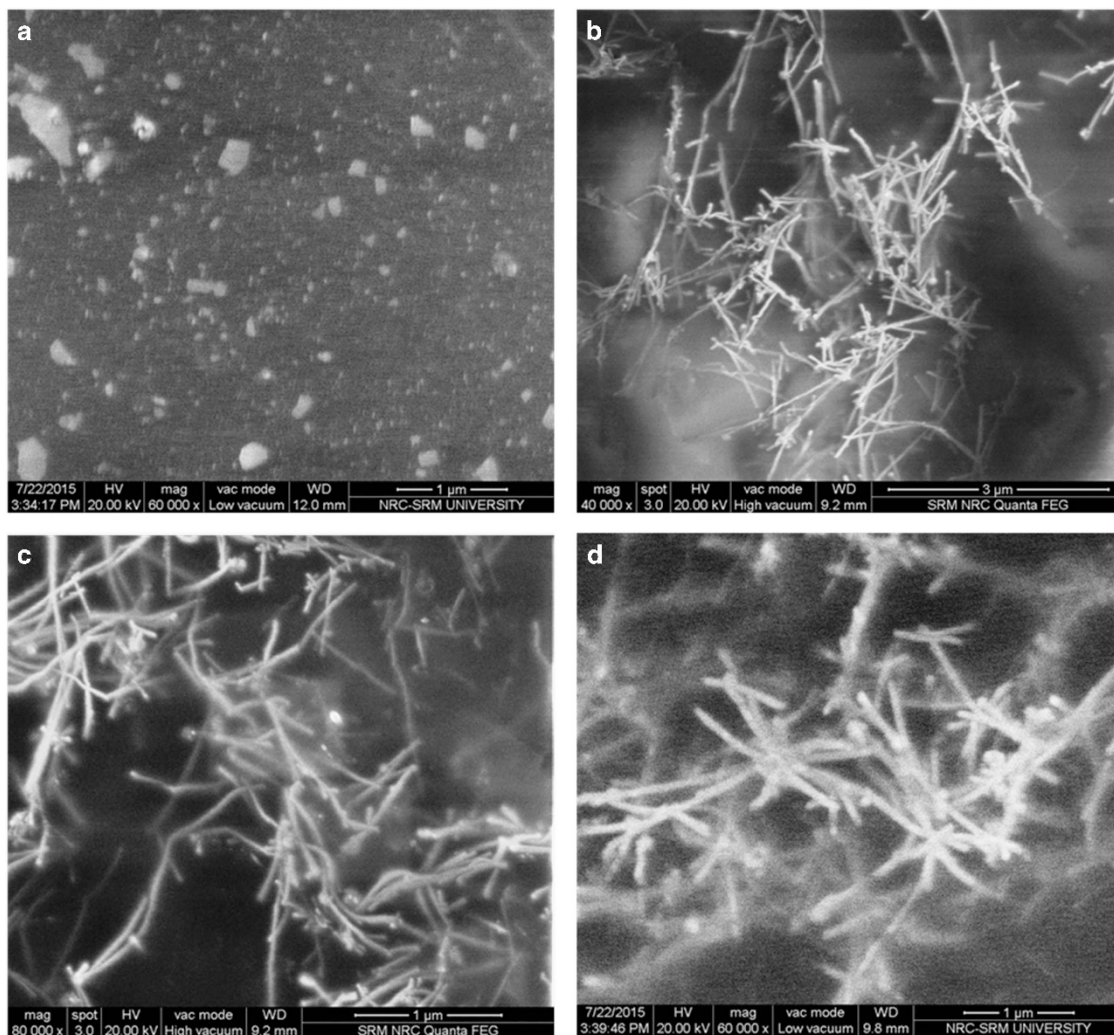
Figure 5 Field emission scanning electron microscopy (FE-SEM) images of (**a**) sulfonated poly (ether ether ketone) (SPEEK), (**b**) SP-CNT-FA-2, (**c**) SP-CNT-FA-4 and (**d**) SP-CNT-FA-6.
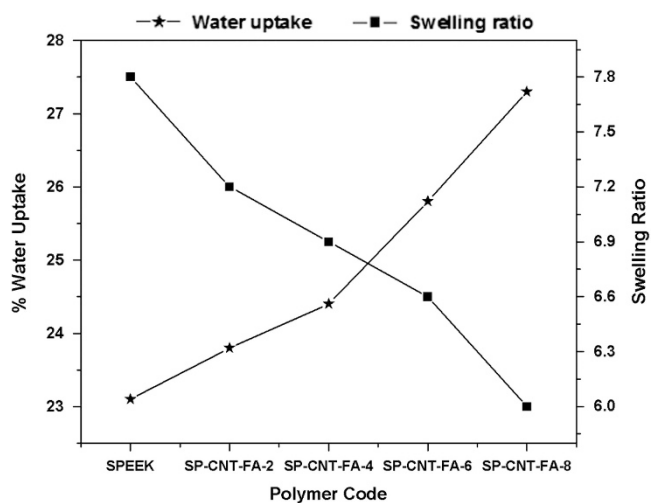

Figure 6 Comparison of water uptake and swelling ratio of the sulfonated poly (ether ether ketone) (SPEEK) and polymer nanocomposites.
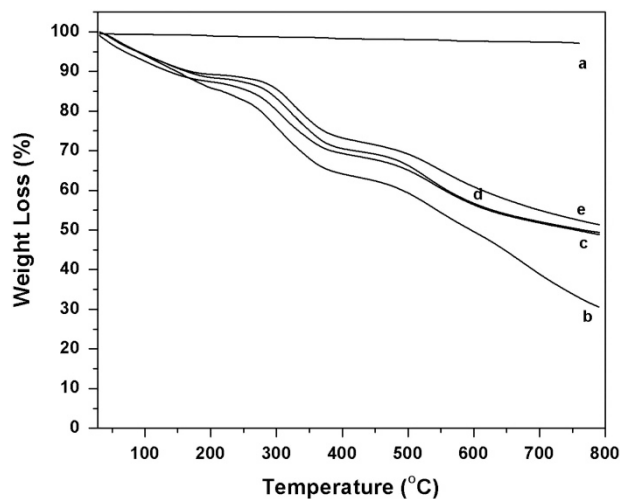

Figure 7 Thermograms of poly (ether ether ketone) (PEEK), sulfonated poly (ether ether ketone) (SPEEK) and polymer nanocomposites.
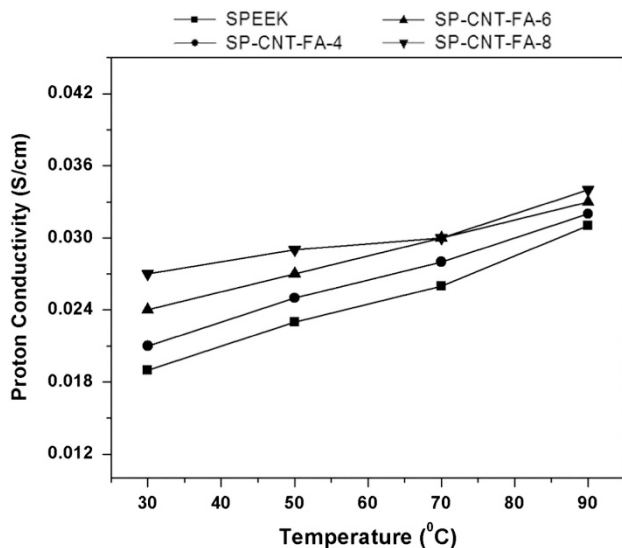
Figure 8 Proton conductivity of sulfonated poly (ether ether ketone) (SPEEK) and polymer nanocomposites.

method. The results shown in Table 2 indicate that the fillers (both SWCNT and fly ash) were well impregnated into the polymer matrix and enhanced the strength of the membranes. The sulfonic acid groups combined with fly ash made the polymer proton not only conducting but also hydrophilic. Hence, the polymer with more sulfonic acid groups swells in humid conditions and loses its mechanical strength, leading to membrane rupture. Therefore, controlling the amount of sulfonic acid groups is of prime importance. In polymer nanocomposites, an increasing concentration of CNTs and fly ash lowers the amount of sulfonic acid content and thereby improves the tensile strength. The SP-CNT-FA-8 membrane exhibits the maximum tensile strength of 74.4 MPa.

Proton conductivity

The performance and efficiency of a fuel cell depend on the proton conductivity of the membrane. Hydrocarbon-based polymers with polar groups exhibit a high water uptake over a wide range of temperatures. The proton conductivities of SPEEK and nanocomposite membranes were determined from 30 to 90 °C and is shown in Figure 8. It can be seen from Figure 8 that the proton conductivity of the prepared membranes increased in the following order: SPEEK < SP-CNT-FA-2 < SP-CNT-FA-4 < SP-CNT-FA-6 < SP-CNT-FA-8.

With an increasing temperature, the dynamics involved in proton transfer and structural reform are faster and more efficient and, hence, lead to a higher proton conductivity. The conductivity results indicate that an increasing concentration of CNT and fly ash in the polymer nanocomposites results in higher proton conductivity. Generally, proton conductivity depends directly on the sulfonic acid content and the water uptake ability of the polymer. However, the presence of sulfonic acid groups in a polymer electrolyte membrane is not always a major factor for increasing the proton conductivity. The ability of the membrane to retain the water clusters in the polymer matrix should be considered because it contributes to the proton conductivity.[40,47]

Electrochemical performance

Membrane electrode assemblies were characterized using a pure hydrogen-oxygen fuel cell system. A comparison of the electrochemical single-cell performances of pristine SPEEK and SP-CNT-FA-6
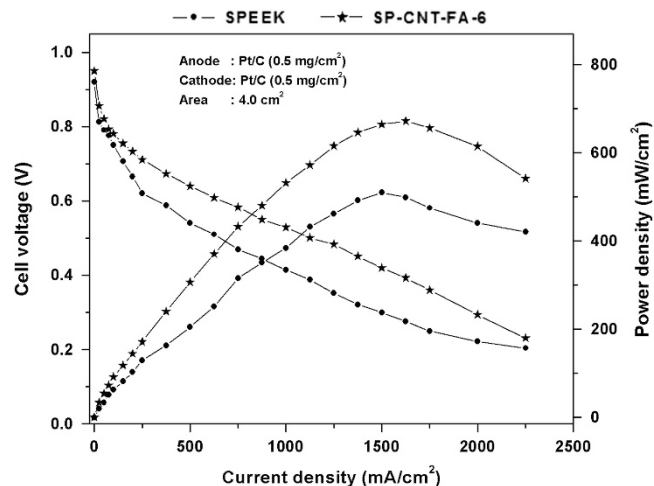

Figure 9 The electrochemical performance of sulfonated poly (ether ether ketone) (SPEEK) and composite membrane at 60 °C and 100% relative humidity (RH).

membranes at 60 °C under 100% relative humidity was carried out. The power density and polarization curves of the electrolyte membranes are shown in Figure 9. The best performance was achieved for the SP-CNT-FA-6 membrane, which produced a peak power density of 672 mW cm^{-2} at a load current density of 1625 mA cm^{-2}, whereas the pristine membrane produced 510 mW cm^{-2} at a load current density of 1500 mA cm^{-2}. The good water uptake capacity and proton conductivity of the nanocomposite membranes are attributed to the better performance of SP-CNT-FA-6 membrane over the entire current density range.

CONCLUSIONS

Organic–inorganic polymer nanocomposite membranes were prepared by including fly ash and SWCNT additives. The structure and physicochemical properties of the nanocomposite membranes were studied in detail. The morphology studies confirm the successful incorporation of CNTs into the polymer matrix. The IEC of the membranes was found to be between 1.59 and 1.86 meq g^{-1}. Although there was a decrease in IEC, the water uptake capacity of the polymer nanocomposites increased by incorporating the inorganic additives, thereby enhancing the proton conductivity of the membranes. Furthermore, membrane electrode assemblies were fabricated for SPEEK and SP-CNT-FA-6 membranes, the latter of which has a maximum peak power density of 672 mW cm^{-2}. An enhancement of thermal stability in the composite membranes may have occurred predominantly because of the incorporation of SWCNTs and fly ash. The excellent thermal and mechanical stability as well as the relatively high proton conductivity of the synthesized membranes make them a better choice for fuel cell applications.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1 Vinayan, B. P., Nagar, R., Rajalakshmi, N. & Ramaprabhu, S. Novel platinum-cobalt alloy nanoparticles dispersed on nitrogen-doped grapheme as a cathode electrocatalyst for PEMFC applications. *Adv. Funct. Mater.* **22**, 3519–3526 (2012).

2 Manabu, T., Masaki, K., Kenji, M. & Masahiro, W. Synthesis and properties of anion conductive ionomers containing fluorenyl groups for alkaline fuel cell applications. *Polym. Chem.* **2**, 99–106 (2011).

3 Costamanga, P. & Srinivasan, S. Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000: Part I. Fundamental scientific aspects. *J. Power Sources* **102**, 242–252 (2001).

4 Gh Park, K. T., Chun, J. W., Kim, S. G., Chun, B. H. & Kim, S. H. Synthesis and characterization of crosslinked sulfonated poly (arylene ether sulfone) membranes for high temperature PEMFC applications. *Int. J. Hydrogen Energy* **36**, 1813–1819 (2011).

5 Yee, R. S. L., Zhang, K. & Ladewig, B. P. The effects of sulfonated poly(ether ether ketone) ion exchange preparation conditions on membrane properties. *Membranes* **3**, 182–195 (2013).

6 Kreuer, K. D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.* **185**, 29–39 (2001).

7 Lu, D., Zou, H., Guan, R., Dai, H. & Lu, L. Sulfonation of polyethersulfone by chlorosulfonic acid. *Polym. Bull.* **54**, 21–28 (2005).

8 Sonpingkam, S. & Pattavarakorn, D. Mechanical properties of sulfonated poly (ether ether ketone) nanocomposite membranes. *Int. J. Chem. Eng. Appl.* **5**, 181–185 (2014).

9 Liu, Y. L. Effective approaches for the preparation of organo-modified multi-walled carbon nanotubes and the corresponding MWCNT/polymer nanocomposites. *Polym. J.* **48**, 351–358 (2016).

10 Wang, L., Kang, J., Nam, J. D., Suhr, J., Prasad, A. K. & Advani, S. G. Composite membrane based on graphene oxide sheets and Nafion for polymer electrolyte membrane fuel cells. *Electrochem. Lett.* **4**, F1–F4 (2015).

11 Maab, H. & Nunes, S. P. Modified SPEEK membranes for direct ethanol fuel cell. *J. Power Sources* **195**, 4036–4042 (2010).

12 Kanakasabai, P., Vijay, P., Deshpande, A. P. & Varughese, S. Crosslinked poly(vinyl alcohol)/sulfonated poly(ether ether ketone) blend membranes for fuel cell applications —surface energy characteristics and proton conductivity. *J. Power Sources* **196**, 946–955 (2011).

13 Ismail, A. F., Othman, N. H. & Mustafa, A. Sulfonated polyether ether ketone composite membrane using tungstosilicic acid supported on silica-aluminium oxide for direct methanol fuel cell (DMFC). *J. Membr. Sci.* **329**, 18–29 (2009).

14 Nunes, S. P., Ruffmann, B., Rikowski, E., Vetter, S. & Richau, K. Inorganic modification of proton conductive polymer membranes for direct methanol fuel cells. *J. Membr. Sci.* **203**, 215–225 (2002).

15 DiVona, M. L., Sgreccia, E., Donnadio, A., Casciola, M., Chailan, J. F., Auer, G. & Knauth, P. Composite polymer electrolytes of sulfonated poly ether ether ketone (sPEEK) with organically functionalized TiO₂. *J. Membr. Sci.* **369**, 536–544 (2011).

16 Ruffmann, B., Silva, H., Schulte, B. & Nunes, S. P. Organic/inorganic composites membranes for application in DMFC. *Solid State Ionics* **269**, 162–163 (2003).

17 Eroglu, I., Sengul, E., Erdener, H., Akay, R. G., Yucul, H. & Bac, N. Effects of sulfonated polyether-ether ketone (s-PEEK) and composite membranes on the proton exchange membrane fuel cell performance. *Int. J. Hydrogen Energy* **34**, 4645–4652 (2009).

18 Hasani-Sadrabadi, M. M., Emami, S. H., Ghaffarian, R. & Moaddel, H. Nanocomposite membranes made from sulfonated polyether-ether ketone and montmorillonite clay for fuel cells applications. *Energy Fuels* **22**, 2539–2542 (2008).

19 Dogan, H., Inan, T. Y., Unveren, E. & Kaya, M. Effect of cesium salt of tungstophosphoric acid (Cs-TPA) on the properties of sulfonated polyether ether ketone (SPEEK) composite membranes for fuel cell applications. *Int. J. Hydrogen Energy* **35**, 7784–7795 (2010).

20 Zaidi, S. M. J. & Ahmad, M. I. Novel SPEEK/heteropolyacids loaded MCM-41 composite membranes for fuel cell applications. *J. Membr. Sci.* **279**, 548–557 (2006).

21 Paradesi, D., Ramanujam, R. A. & Jaisankar, S. N. Synthesis and characterization of sulfonated poly (arylene ether sulfone) (SPAES)/silicotungstic acid (STA) composite membranes for fuel-cells. *Polym. J.* **45**, 166–172 (2013).

22 Ismail, A. F., Mohtar, S. S. & Matsuura, T. Preparation and characterization of sPEEK/MMT-STA composite membrane for DMFC application. *J. Membr. Sci.* **371**, 10–19 (2011).

23 Klingele, M., Breitwieser, M., Zengerleab, R. & Thiele, S. Direct deposition of proton exchange membranes enabling high performance hydrogen fuel cells. *J. Mater. Chem. A* **3**, 11239–11245 (2015).

24 Wehkamp, N., Breitwieser, M., Büchler, A., Klingele, M., Zengerle, R. & Thiele, S. Directly deposited Nafion/TiO₂ composite membranes for high power medium temperature fuel cells. *RSC Adv.* **6**, 24261–24266 (2016).

25 Meenakshi, S., Sahu, A. K., Bhat, S. D., Sridhar, P., Pitchumani, S. & Shukla, A. K. Mesostructured-aluminosilicate-Nafion hybrid membranes for direct methanol fuel cells. *Electrochim. Acta* **89**, 35–44 (2013).

26 Kannan, R. & Pillai, V. K. Applications of carbon nanotubes in polymer electrolyte membrane fuel cells. *J. Indian Inst. Sci.* **89**, 425–436 (2009).

27 Tripathi, B. P. & Shahi, V. K. Organic–inorganic nanocomposite polymer electrolyte membranes for fuel cell applications. *Prog. Polym. Sci.* **36**, 945–979 (2011).

28 Ismail, A. F., Rahim, N. H., Mustafa, A., Matsuura, T., Ng, B. C., Abdullah, S. & Hashemifard, S. A. Gas separation performance of polyethersulfone/multi-walled carbon nanotubes mixed matrix membranes. *Sep. Purif. Technol.* **80**, 20–31 (2011).

29 Kim, D. J., Jo, M. J. & Nam, S. Y. A review of polymer–nanocomposite electrolyte membranes for fuel cell application. *J. Ind. Eng. Chem.* **25**, 36–52 (2015).

30 Murali, A., Senthil, A. G. T., Jaisankar, S. N. & Mandal, A. B. Augmentation of properties on sparingly loaded nanocomposites *via* functionalized single-walled carbon nanotubes using a covalent approach. *RSC Adv.* **4**, 62947–62950 (2014).

31 Anandan, S. Recent trends in fly ash utilization in polymer composites. *Int. J. Waste Resour.* **4**, 1000149 (2014).

32 Blissett, R. S. & Rowson, N. A. A review of the multi-component utilization of coal fly ash. *Fuel* **97**, 1–23 (2012).

33 Parvaiz, M. R., Mohanty, S., Nayak, S. K. & Mahanwar, P. A. Effect of surface modification of fly ash on the mechanical, thermal, electrical and morphological properties of poly ether ether ketone composites. *Mater. Sci. Eng. A* **528**, 4277–4286 (2011).

34 Nath, D. C. D., Bandyopadhyay, S., Boughton, P., Yu, A., Blackburn, D. & White, C. Chemically modified fly ash for fabricating super-strong biodegradable poly(vinyl alcohol) composite films. *J. Mater. Sci.* **45**, 2625–2632 (2010).

35 Manoj, S. & Vikas, C. Mechanical properties of epoxy resin–fly ash composite. *J. Miner. Mater. Character. Eng.* **9**, 199–210 (2010).

36 Zaidi, S. M. J., Mikhailenko, S. D., Robertson, G. P., Guiver, M. D. & Kaliaguine, S. Proton conducting composite membranes from poly ether ether ketone and heteropolyacids for fuel cell applications. *J. Membr. Sci.* **173**, 17–34 (2000).

37 Gil, M., Ji, X., Li, X., Na, H., Hampsey, J. E. & Lu, Y. Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications. *J. Membr. Sci.* **234**, 75–81 (2004).

38 Paradesi, D. & Ramanujam, R. A. sulfonated poly(ether ether ketone) and poly(ethylene glycol) diacrylate based semi-interpenetrating network membranes for fuel cells. *J. Macromol. Sci. Part A* **49**, 191–200 (2012).

39 Muthu Lakshmi, R. T. S., Choudhary, V. & Varma, I. K. Sulfonated poly(ether ether ketone): synthesis and characterisation. *J. Mater. Sci.* **40**, 629–636 (2005).

40 Paradesi, D., Samanta, D., Mandal, A. B. & Jaisankar, S. N. A novel fuel cell membrane with high efficiency. *RSC. Adv.* **4**, 26193–26200 (2014).

41 Zing, P., Robertson, G. P., Guiver, M. D., Mikhailenko, S. D., Wang, K. & Kaliaguine, S. Synthesis and characterization of sulfonated poly (ether ether ketone) for proton exchange membranes. *J. Membr. Sci.* **229**, 95–106 (2004).

42 Robertson, G. P., Mikhailenko, S. D., Wang, K., Xing, P., Guiver, M. D. & Kaliaguine, S. Casting solvents interactions with sulfonated poly (ether ether ketone) during proton exchange membrane fabrication. *J. Membr. Sci.* **219**, 113–121 (2003).

43 Uma, T., Suresh, K., Akira, K. & Kunio, K. Synthesis of organic/inorganic hybrid composite membranes and their structural and conductivity properties. *Mater. Lett.* **72**, 81–87 (2012).

44 Klaysom, C., Ladewig, B. P., Lu, G. Q. M. & Wang, L. Preparation and characterization of sulfonated polyethersulfone for cation-exchange membranes. *J. Membr. Sci.* **368**, 48–53 (2011).

45 Salgado, J. R. Study of basic biopolymer as proton membrane for fuel cell systems. *Electrochim. Acta* **52**, 3766–3778 (2007).

46 Tripathi, B. P., Schieda, M., Shahi, V. K. & Nunes, S. P. Nanostructured membranes and electrodes with sulfonic acid functionalized carbon nanotubes. *J. Power Sources* **196**, 911–919 (2011).

47 Muthumeenal, A., Neelakandan, S., Kanagaraj, P. & Nagendran, A. Synthesis and properties of novel proton exchange membranes based on sulfonated polyethersulfone and *N*-phthaloyl chitosan blends for DMFC applications. *Renewable Energy* **86**, 922–929 (2016).