Ionics (2019) 25:2243–2253
https://doi.org/10.1007/s11581-018-2613-4

ORIGINAL PAPER

Influence of barium zirconate on SPEEK-based polymer electrolytes for PEM fuel cell applications

K. Selvakumar[1] · S. Rajendran[1] · M. Ramesh Prabhu[1]

Received: 1 April 2018 / Revised: 23 May 2018 / Accepted: 28 May 2018 / Published online: 12 June 2018

Abstract

The sulfonated poly(ether ether ketone) (SPEEK)-barium zirconate ($BaZrO_3$)-based polymer nanocomposite membranes are prepared by solvent casting technique. The composite membranes have been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), water uptake, swelling, and ion exchange capacity (IEC). The NMR, IEC, and CHNSO analyses confirmed the degree of sulfonation level of SPEEK as 65%. Addition of 6 wt% $BaZrO_3$ filler improved the proton conductivity of the polymer electrolyte considerably with 3.12×10^{-1} S/cm at 90 °C. SEM and AFM studies indicated that the $BaZrO_3$ nanofillers are well distributed in the polymer up to 8 wt%. The maximum power and current density are 183 mW cm^{-2} and 280 mA cm^{-2} for 94 wt% SPEEK and 06 wt% $BaZrO_3$. It is concluded that the above composite membrane is a potential candidate for PEM fuel cell applications.

Keywords PEM · SPEEK · Thermal stability · NMR · AFM

Introduction

Proton exchange membrane fuel cells are considered as environmentally friendly because decreasing of long-term dependence on oil and other fossil fuels are in the alternative source of energy [1]. It also has attracted extensive attention because of potential application in portable electronic devices such as fuel cells, batteries, electrolysis, desalinations, and separations [2–6]. The proton exchange membrane fuel cells (PEMFCs) are one of the most important applications of PEM, which have promising power applications such as vehicular applications [7]. PEMFCs have lot of benefits such as high-temperature operation, environmentally friendly, high energy density, and appropriate fuel cell storage [8]. For the above applications, lots of PEM have been developed. Nowadays, Nafion is a benchmark material used in PEMFCs. Some major draw backs are available in the Nafion such as it cannot operate at high temperature, water management problem, high cost, and low mechanical stability. Since recent years, there has been an effort to develop a low-cost inorganic and organic polymer composite membrane. In recent years, several kinds of proton exchange membranes such as sulfonated poly(ether sulfone) (PES) [9], sulfonated poly(arylene ether sulfone) [10], and sulfonated poly(benzimidazole) [11] have been studied. In hybrid organic-inorganic composite membranes, the inorganic part usually offers good thermal and mechanical stability, while the organic functional groups such as SO_3H gives specific chemical reactivity [12]. The aromatic hydrocarbon polymer poly(ether ether ketone) is a semi-crystalline polymer that has a high chemical and thermal stability. It is a high-performance thermostable engineering polymer with non-fluorinated backbone. The proton conductivity of sulfonated poly(ether ether ketone) (SPEEK) can be easily controlled by the degree of sulfonation (DS) and DS can be balanced by sulfonation criteria such as reaction time, temperature, and concentration of sulfuric acid. In order to give hydrophilicity in the pure PEEK polymer, it is sulfonated with the help of sulfuric acid. The hydrophilic/hydrophobic phase separation in SPEEK is narrower and more branched, which results in low electroosmotic drag and low methanol permeation [13, 14]. Sulfonated poly (ether ether ketone) displays numerous advantages such as excellent film-forming property, excellent thermal stability, high mechanical strength, and sufficient proton conductivity that all depend upon the degree of sulfonation. To this end, the membranes require to be suitably

---

✉ M. Ramesh Prabhu
mkram83@gmail.com

[1] Department of Physics, Alagappa University, Karaikudi 630 004, India

composed with hygroscopic fillers such as TiO_2, SiO_2, Fe_2O_3, and alumina nanostructures which have been largely studied over the past decade for use in PEM of high-temperature fuel cells [15–18]. Nowadays, perovskite structured materials are required in the fuel cell. Proton conductors with ABO_3 structure have been particularly studied due their high proton conductivity, moderate chemical stability, and excellent mechanical and thermal stability. The perovskite currently expressed by ABO_3 is structurally stable because of its well-balanced geometrical array of constituent atoms and their valences [19]. Perovskites can be synthesized with a widespread variation of array of chemical elements because cations of large site (A) and small (site B) ionic radius are well suitable in crystalline structures. Perovskite structures from group II elements such as Sr, Ba, and Ra can be used as hygroscopic materials to improve the humidity sensing. So perovskite materials are predominantly proton conductors at high temperatures. Recently, barium zirconate is widely used for proton exchange membrane fuel cells. $BaZrO_3$ is a well-known proton conductor with ABO_3 perovskite structure which has lattice parameter of $a = 4.2$ Å, high melting point, a small thermal coefficient, and excellent mechanical and thermal stability. $BaZrO_3$ is a well-known refractory material with very high melting point (2600 °C) and low chemical reactivity toward corrosive compounds [20]. It has excellent thermal stability and resistance due to a low coefficient of thermal expansion ($\alpha = 87 \times 10^{-7}$/°C). In the present work, SPEEK-based nanocomposite membranes are prepared by solvent casting technique and characterized by XRD, FTIR, NMR, IEC, etc. The best composite membrane has been identified in terms of current density and power density applications.

Experimental

Materials and method

Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4 phenylene) (PEEK; Mw = 20,800, Victrex (USA)), *N*-methyl-2-pyrrolidone) (NMP; 99%), concentrated sulfuric acid (H_2SO_4) (98%), and methanol (99%) were purchased from SRL (India), and barium nitrate (99.8%), zirconium nitrate (99%), and cetyltrimethylammonium bromide (95%) were procured from Alfa Aesar (India).

Sulfonation reaction process

Ten grams of PEEK was added into 200 mL of sulfuric acid and the mixture was subjected to vigorous stirring under the N_2 atmosphere at room temperature for 7 h. The obtained solution was poured into ice-cold deionized water to precipitate the sulfonated polymer (SPEEK), followed by filtration and thorough washing of the filtrate using deionized water until neutral pH was obtained. It is important to remove even the last trace of acid as it may affect the product. The obtained SPEEK was dried in a vacuum oven at 90 °C for 24 h [21]. The synthesis process can be explained by Scheme 1.

Synthesis of $BaZrO_3$

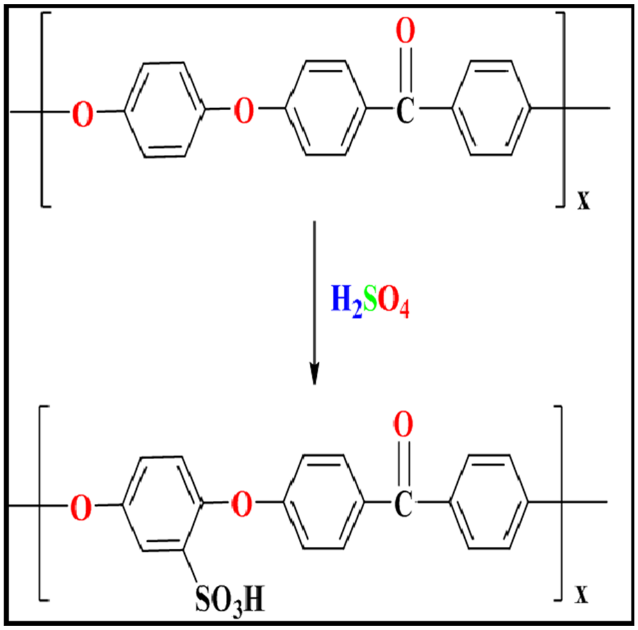
Barium nitrate (2 g), zirconium nitrate (1 g), and cetyltrimethylammonium bromide were dissolved in a solution of ethanol water solution at room temperature and the resultant solution was vigorously stirred for 30 min. Under strong stirring, sodium hydroxide was added and the solution was stirred again for 1 h at room temperature. The hydrothermal reaction was carried out in a Teflon autoclave under the autogenous pressure. For different reaction times, the precipitate was then washed with distilled water and dried in oven at 100 °C followed by calcination at 1000 °C [22].

Polymer nanocomposite membranes

SPEEK was dissolved in 20 mL of NMP under continuous stirring to form a homogeneous viscous solution. Interaction of typical SPEEK-$BaZrO_3$ composite took place when $BaZrO_3$ is added into the solution. The resulting solution was cast in a petri dish and the solvent was evaporated at 70 °C under vacuum for 14 h. The thicknesses of the membranes were found to be ~ 160 μm.

Pre-treatment of membrane

The membranes were immersed in 1 M H_2SO_4 solution for 4 h at 30 °C to activate the acidic functional groups. Finally, those



Scheme 1 Sulfonation process for SPEEK

activated in the membranes were immersed in DI water for 24 h to remove the free acid [23].

Instrument and apparatus details

The crystallinity of the proton-conducting polymer electrolytes was studied by XRD pattern with the help of X'Pert PRO PANalytical X-ray diffractometer. The complex formation between SPEEK and $BaZrO_3$ was identified by FTIR spectrophotometer in the range of 400–4000 cm^{-1}. NMR spectra were recorded on a Bruker 500 MHZ NMR spectrometer. Morphology of the composite membrane was examined by a high-resolution scanning electron microcopy (HRSEM) (FEI Quanta 250 microscope, Netherlands). Thermal stability of the polymer electrolytes was carried out using TGA model (SDT Q600) by heating under N_2 atm. The surface topography and roughness factor of the sample were observed by atomic force microscope with the help of AFM (A100SGS). The elemental analysis was carried out using CHNSO elemental analyzer using elemental Vario EL III Germany. A catalyst ink was prepared by a conventional method. A combination of 0.2 g platinum nominally 40% on carbon black (Alfa Aesar), 6 g of isopropanol, and 5 wt% Nafion solution was mixed in catalyst ink slurry that was mixed in an ultrasonic bath overnight to reduce the catalyst powder and got in a homogeneous ink. Catalyst membranes were prepared by hand painting this catalyst ink that was applied on both sides of the membrane with an air brush. The Pt:C loading was 0.5 mg cm^{-2} for both sides of the membrane. The composite membrane was then sandwiched between the electrodes by hot pressing [24]. MEAs with an active area of 5 cm^{-2} were prepared by incorporating two gas diffusion layers (GDL sigracet GDL 10BB, 420 μm, SGL carbon group) on both sides of the catalyzed membrane and flow field is serpentine type. The evaluation of fuel cell performance at 90 °C by using fuel cell model 850e (Scribner Associates, Inc.). The polarization curves were recorded at atmospheric pressure using humidified oxygen (0.2 L min^{-1}) and hydrogen (0.2 L min^{-1}) with dry conditions. Polarization curves were obtained by using current step potentiometry.

Measurements

Proton conductivity

The prepared polymer composite was subjected to AC impedance analysis in order to calculate the proton conductivity with the help of computer-controlled microautolab type III potentiostat/galvanostat in the frequency range of 100 Hz–300 KHz over the temperature range of 303–353 K. The following equation was used for the calculation of proton conductivity:

$$\sigma = \frac{l}{R_b A}$$

where $A = 3.14$ cm^2 is the cross-sectional area of the membrane, l is the thickness of the membrane, and R_B is the bulk resistance. The measurement was taken at different temperatures respectively.

Water uptake and swelling ratio

Water uptake and swelling ratio of the composite membranes were performed by dipping the composites in water for 2 days. The prepared polymer composite membranes were dried in vacuum oven for 24 h at 80 °C. The prepared composite membranes were dipped in distilled water to determine the water uptake of the membrane. Weight of the wet membranes was measured after drying the sample overnight in a vacuum at 80 °C. The water uptake of the membrane was calculated from the following equation

$$\text{Water uptake } (\%) = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}\right) \times 100$$

Here W_{wet} and W_{dry} are the weight of the wet and dry membranes respectively.

The swelling ratios of the membranes were calculated as follows:

$$\text{Swelling ratio } (\%) = \left(\frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}}\right) \times 100$$

where L_{Wet} and L_{Dry} are the lengths of the wet and dry membranes respectively.

Ion exchange capacity

Classical back titration technique was used to determine the IEC of the membranes. First, the membranes in the acid form (H^+) were converted to sodium form by immersing the membranes in 1 M NaCl solution for 24 h at 40 °C [25]. Then the exchanged H^+ ions within the solutions were titrated with 0.0 1 M NaOH solution using phenolphthalein as an indicator [26]. The IEC values (meq g^{-1}) of the membranes can be calculated from the following equation:

$$IEC = \frac{(V_{\text{NaOH}})(N_{\text{NaOH}})}{W_{\text{dry}}}$$

where V_{NaOH} is the volume of NaOH solution, N_{NaOH} is the normality of NaOH solution, and W_{dry} is the mass of the dry sample.

Oxidative stability

The chemical stability was measured by measuring the weight loss of the proton-conducting composite membrane (2 × 2 cm) in Fenton's solution (3 wt% H_2O_2 containing 2 ppm $FeSO_4$) at 60 °C for 1 day.

Results and discussion

Degree of sulfonation

(A) IEC

The degree of sulfonation (DS) is defined as the percentage of repeating units of PEEK that has been sulfonated and calculated by using the following equation.

$$DS(\%) = \frac{M_{\mathrm{PEEK}} \times IEC \times 100}{(1000-(M_{\mathrm{SPEEK}}-M_{\mathrm{PEEK}}) \times IEC)}$$

M_{PEEK} and M_{SPEEK} are the molecular weights of PEEK and SPEEK repeating units and the values are 288 and 368 respectively [27] [28] by substituting these values into the above equation. The number (80) resulted from the difference between these two unit molecular weights.

$$DS(\%) = \frac{288 \times IEC \times 100}{(1000-80 \times IEC)}$$

The degree of sulfonation was found to be 65%.

(B) Nuclear magnetic resonance spectroscopy

Figure 1 represents hydrogen-nuclear magnetic resonance (^{1}H) spectroscopy that was used to calculate the DS and it was calculated using comparative integration of distinct aromatic signals according to the following equation:

$$\frac{n}{12-2n} = \frac{SH_{13}}{\sum SH_{(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15)}} \quad (0 \leq n \leq 1)$$

where n is the number of H_{13} repeat unit. SH_{13} is the area under the graph for H_{13} region and integrated peak area $\sum SH_{(1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15)}$ of the signals corresponding to all aromatic hydrogen [29]. The degree of sulfonation is obtained by the equation

$$DS = n \times 100\%$$

The presence of sulfonic acid group causes a characteristic singlet (H_{13}) at 7.5 ppm.

The DS obtained was 65% for the prepared SPEEK

(C) C H N S O analyzer

The elemental content of the membrane is reported as weight percentage. Carbon is 65.5%, hydrogen 5.23%, sulfur 4.95%, and empirical formulae $C_{35}H_{34}O_{10}S_1$. From the sulfur content, the DS was calculated by the following equation:

$$DS = \frac{S_E \times 100}{S_T}$$

where S_{E} and S_T represents the experimental and theoretical value of ($-SO_3$ H) per repeat unit of PEEK and sulfur content of PEEK [30]. The DS is calculated as 65% for the prepared SPEEK.

XRD analysis

A phase change helps to take obtain from XRD analysis due to the polymer sulfonation and addition of $BaZrO_3$ nanoparticles in the polymer composites. Figure 2(A–G) shows the XRD pattern of PEEK, SPEEK, $BaZrO_3$, and polymer composite membrane. From Fig. 2(F), four major peaks of pure PEEK are found at $2\theta = 18.87°$, 20.7°, 23°, and 28.9° which correspond to the diffractions of (110), (111), (200), and 211 crystalline planes [31]. Sulfonation of PEEK changes the chain conformation and thus brings about loss of crystallinity which reveals a mixture of both amorphous and crystalline nature with a broad peak at 20°. Figure 2(A) shows the XRD pattern of $BaZrO_3$ nanoparticle. Characteristic peaks at $2\theta = 30.11°$, 37.10°, 43.10°, 48.51°, 53.49°, 62.61°, 71.03°, 75.08°, and 79.08° confirmed the presence of $BaZrO_3$ [21]. Figure 2(B–E) reveals that the amorphous nature of SPEEK increased with the incorporation of the $BaZrO_3$ nanoparticles; the degree of crystallinity is calculated using the relation

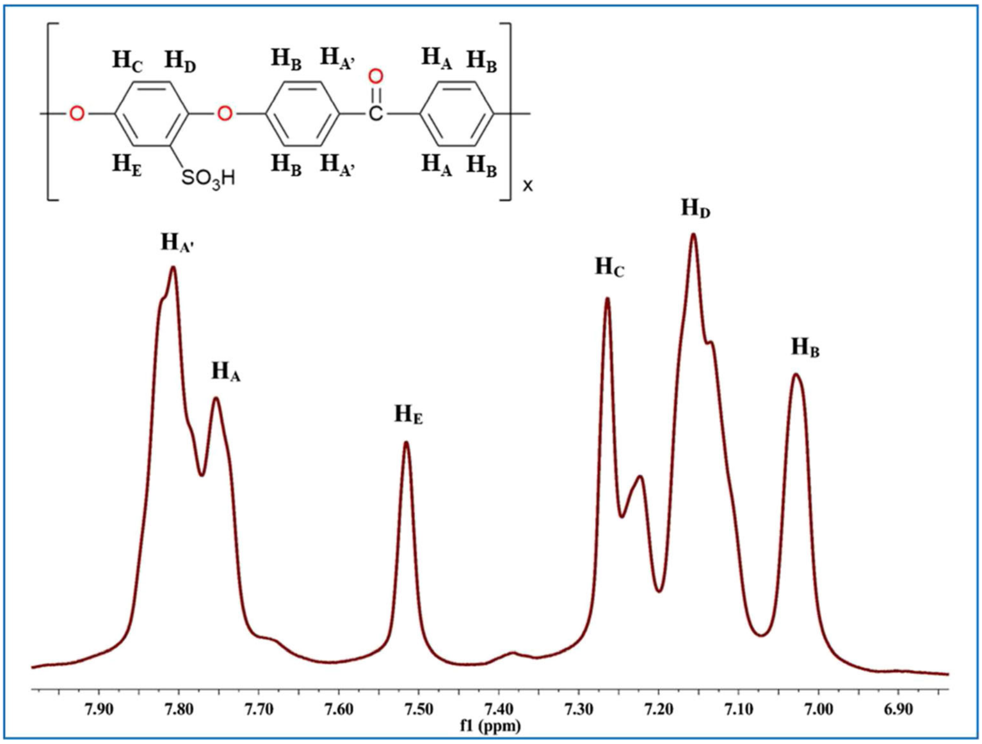
$$K = \frac{S}{S0} \times 100\%$$

where s denotes sum of areas of all the crystalline peaks and s_0 represents sum of areas of crystalline peaks and amorphous hump. The SPEEK corresponds to the crystallinity value of 3.368%. It is seen that the percentage of crystallinity of the nanocomposite membranes decreased up to 6 wt% of $BaZrO_3$. For the prepared samples A, B, C, and D, the degree of crystallinity is found to be 2.102, 1.132, 0.956, and 1.323% respectively. Hence, the absence of peaks pertaining to $BaZrO_3$ in the complexes indicates the thorough mixing of nanoparticle in the polymer matrix is completely dispersed. In 8 wt% $BaZrO_3$ in the prepared polymer composite, the peak intensity increases due to aggregation of $BaZrO_3$ nanoparticles that has occurred within the polymer matrix.

FTIR analysis

Figure 3(A–C) shows the FTIR spectra of PEEK, SPEEK, and $BaZrO_3$. The vibrational peaks observed at 1655 cm^{-1} (C=O), 1509 cm^{-1} (–CH), 1244 cm^{-1} (C–O–C), and 1484 cm^{-1} (C–

Fig. 1 ^{1}Proton NMR Spectrum of SPEEK



C) are the characteristic peaks of PEEK. The peak identified at 1484 cm^{-1} indicates the presence of C–C aromatic ring [32]. The presence of broadband observed at 3427 cm^{-1} is assigned to the O–H stretching vibration of sulfonic acid groups. The vibrational bands related to the sulfonic acid groups appearing at 1220 cm^{-1} (asymmetric O=S=O), 1082 cm^{-1} (symmetric O=S=O), 1024 cm^{-1} (S=O) stretching, and 710 cm^{-1} (S–O) stretching confirm the successful synthesis of SPEEK [33]. The presences of vibrational bands at 400–750 cm^{-1} correspond to the metal–oxygen stretching vibrations of ABO$_3$ perovskite [34]. The small peaks around 2350 cm^{-1} observed in the sample may be to atmospheric CO$_2$. Figure 4(A, B) represents the FTIR spectra of 98 wt% SPEEK-02 wt% BaZrO$_3$ and 94 wt% SPEEK-06 wt% BaZrO$_3$ respectively. The vibrational peaks observed at 1640–1650 and 3450 cm^{-1} are due to bending water molecule present in the prepared polymer electrolytes. The absorption peak at 3450 cm^{-1} is present in all the prepared composites. The vibrational peaks observed at 1020 and 1078 cm^{-1} are attributed

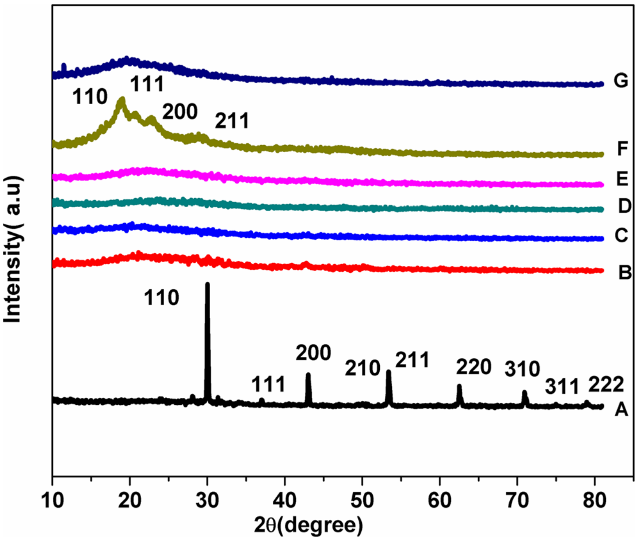


Fig. 2 XRD spectra for (A) BaZrO$_3$, (B) 98 SPEEK-02 BaZrO$_3$, (C) 96 SPEEK-04 BaZrO$_3$, (D) 94 SPEEK-06 BaZrO$_3$, (E) 92 SPEEK-08 BaZrO$_3$, (F) PEEK, G-SPEEK

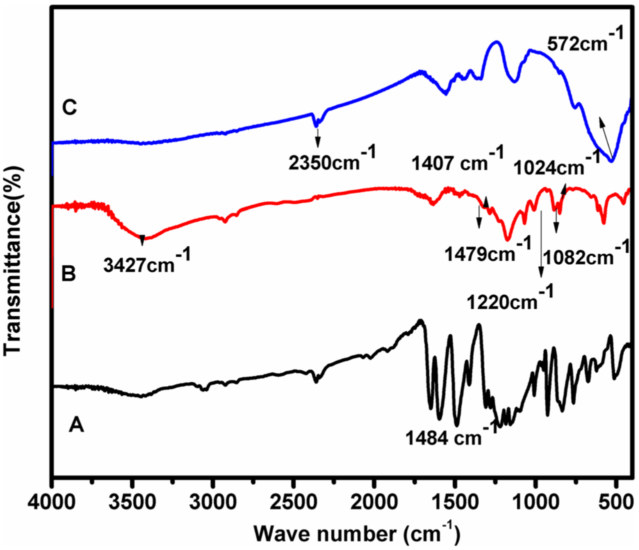


Fig. 3 FTIR spectra for (A) PEEK, (B) SPEEK, and (C) BaZrO$_3$

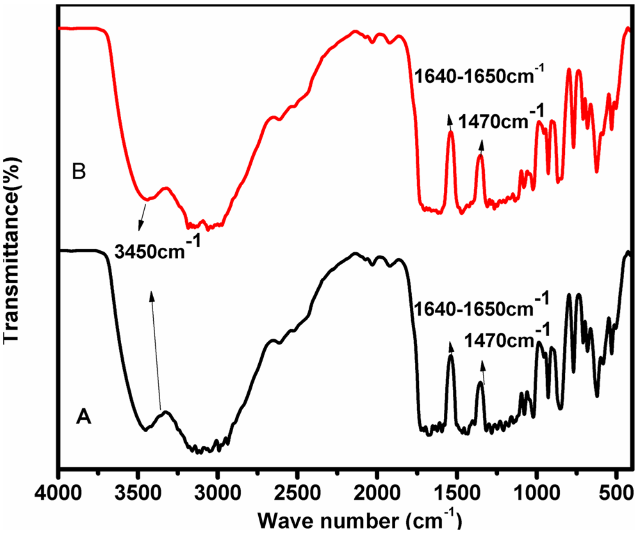


Fig. 4 FTIR spectra for (A) 98 SPEEK-02 $BaZrO_3$ and (B) 94 SPEEK-06 $BaZrO_3$

to the S=O=S vibrations. The vibrational peak observed at 1470 cm^{-1} may be attributed to C=C stretching of the aromatic ring [35]. The absorption peak at 1645 cm^{-1} corresponds to the carbonyl group of SPEEK. In the prepared polymer composites, the peaks at 400–750 cm^{-1} are observed at metal–oxygen stretching vibrations at the B site of ABO_3 perovskite. The present polymer electrolyte is due to the formation of hydrogen bonds between sulfonic acid group of SPEEK and functional group of $BaZrO_3$.

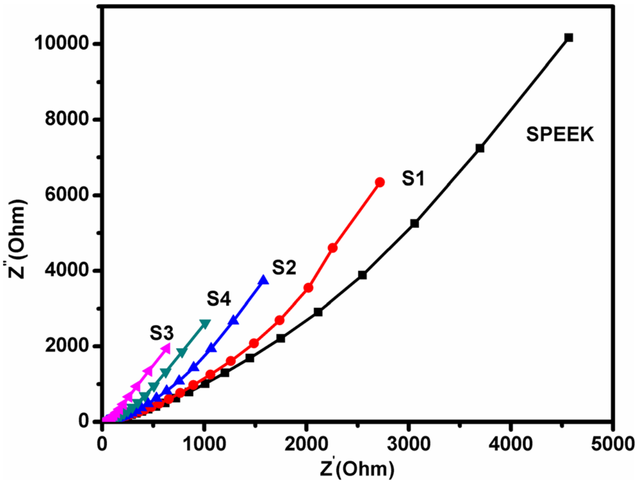


Fig. 5 Nyquist plot for SPEEK and prepared polymer composite at RT

Physico-chemical properties (water uptake, swelling, and IEC properties)

Water uptake is one of the important properties for PEMs, which plays an important role in proton transport. The water uptake for the sulfonated polymer also increases with increasing amount of degree of sulfonation. Water uptake, swelling, and IEC values are shown in Table 1. Water uptake of the SPEEK membrane has been obtained as 35.2% at room temperature with the incorporation of $BaZrO_3$. Water uptake of the nanocomposite membrane is increased due to water retention character and hydrophilic nature of the nanoparticle which is due to the formation of hydrogen bonding between the surfaces of the nanoparticle. However, 08 wt% filler content water uptake started decreasing due to the crystallization in the polymer matrix [36]. The membrane swelling is another important property of composites to specify the dimensional stability of PEMs. The composite with a high membrane swelling lead to low mechanical stability and low durability and it will decrease the cell performance. The swelling of the composite membrane decreased with the addition of $BaZrO_3$ nanoparticle. Similar results have been observed in SPEEK-based composites in the literature [37]. Electrochemical properties of the composite mainly depend on the IEC and water uptake. IEC value depends on the concentration of sulfonic acid group present in the polymer electrolytes. At higher level (08 wt%) $BaZrO_3$, the IEC value is decreased in the system due to the particle agglomeration and blocking effect of BaZrO3 nanoparticles.

AC impedance analysis

Proton conductivity is one of the most important properties which enable membranes to be applicable in PEMFC. Proton conductivities of SPEEK and nanocomposite membranes are shown in Fig. 5. It is found that 94 wt% SPEEK-06 wt% $BaZrO_3$ membrane exhibits high proton conductivity value as 3.12×10^{-1} S/cm at 90 °C. As temperature increases, the proton conductivity values are found to increase. $BaZrO_3$ nanoparticles have proton conduction, which results from their ability to dissolve protons from water in wet atmospheres [38]. Protons are incorporated into $BaZrO_3$ nanoparticles by

Table 1 The water uptake, membrane swelling, and IEC values for prepared polymer composites

Sample code	SPEEK	$BaZrO_3$	IEC (meq/g)	Water uptake (%)	Swelling (%)
A	100	0	1.82	35.2	11.2
B	98	02	1.90	39	10.3
C	96	04	1.95	40	9.8
D	94	06	1.96	41.5	9.7
E	92	08	1.77	26.8	9.9

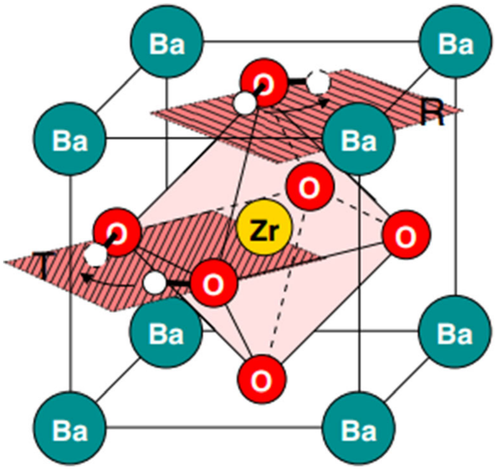


Fig. 6 Schematic illustration of the proton pathway in $BaZrO_3$

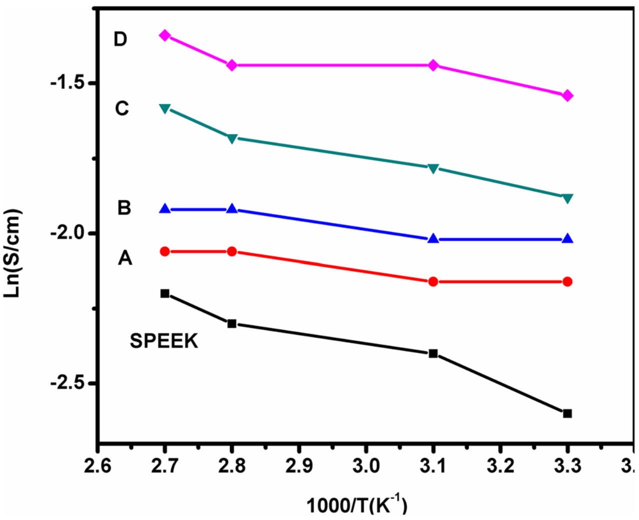


Fig. 7 Arrhenius plot for pure SPEEK and prepared polymer electrolytes

dissociative adsorption of water molecules at the surface, followed by diffusion toward the inner nanoparticles. There are three proton conduction pathways in cubic $BaZrO_3$ such as three-dimensional O–H rotations across Zr_4O_4 square and two-dimensional O–H rotations within Zr_4O_4 square and O–O diagonal path. The schematic design of the proton transfer (T) and reorientation (R) pathways in cubic structure of BaZrO3 are displayed in Fig. 6. In the Grotthuss mechanism for proton transport in $BaZrO_3$ nanoparticles, proton diffuses by an arrangement between a molecular reorientation (R) round the oxygen and jump of the proton from oxygen and it jumps from oxygen to the nearest neighboring ions [39]. The orientation of the O–H group directs the proton near the neighboring oxygen ion. The activation barrier for rotational diffusion is commonly low and hence these rotations are facile. The rotation period to a complete revolution is about 10–12 s and jumping time is about 9–10 s in which it is considered as the limiting step of conduction mechanism [40, 41]. In this case, an oxygen vacancy would be filled by hydroxide group from water dissociation, whereas the proton forms chemical bonding with lattice oxygen. The prepared polymer electrolyte using 94 wt% SPEEK-6 wt% $BaZrO_3$ exhibits the highest proton conductivity. At 8 wt% $BaZrO_3$, the proton conductivity is formed to decrease in the system due to the self-aggregation of $BaZrO_3$ nanoparticles leading to decrease of the active surface of the nanoparticles, and hence, the proton conductivity of the composite membrane also decreased.

Temperature-dependent conductivity

For a hopping-like conduction mechanism, the conductivity follows the Arrhenius behavior.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

where σ is the proton conductivity of the membrane (S cm^{-1}), E_a is the proton-conducting activation energy (KJ mol^{-1}), k_B is a Boltzmann constant, T is temperature, and σ_0 is pre-exponential factor. Arrhenius plots of temperature-dependent proton conductivity are shown in Fig. 6, and the conductivity values are shown in Table 2. The activation energies of proton conductivity are calculated from the slope of the Arrhenius plots. The activation energy often indicates the prevailing mechanism for proton transport. The proton conduction mechanism of SPEEK-$BaZrO_3$ is explained by a Grotthuss mechanism. From Fig. 7, the activation energy is found to decrease with increasing $BaZrO_3$ nanoparticles from 12.01 to 10.61 KJ/mol. This indicates easier proton transfer with increase of $BaZrO_3$. Improvement in the proton conductivity of nanocomposite membranes is belonging to interconnection of hygroscopic $BaZrO_3$ with OH moieties in the polymer matrix and water channeling at the polymer/perovskite interface which can create more pathways for proton transfer. Hence, it is concluded that the proton transport in the SPEEK and

Table 2 Proton conductivity of prepared composites

Sample code	SPEEK	$BaZrO_3$	303 K	323 K	343 K	363 K
A	100	0	2.21×10^{-2}	3.34×10^{-2}	4.32×10^{-2}	5.41×10^{-2}
B	98	02	5.92×10^{-2}	6.01×10^{-2}	6.52×10^{-2}	7.02×10^{-2}
C	96	04	7.51×10^{-2}	7.90×10^{-2}	8.01×10^{-2}	9.01×10^{-2}
D	94	06	1.31×10^{-1}	1.41×10^{-1}	2.51×10^{-1}	3.12×10^{-1}
E	92	08	4.03×10^{-2}	3.54×10^{-2}	3.39×10^{-2}	2.21×10^{-2}

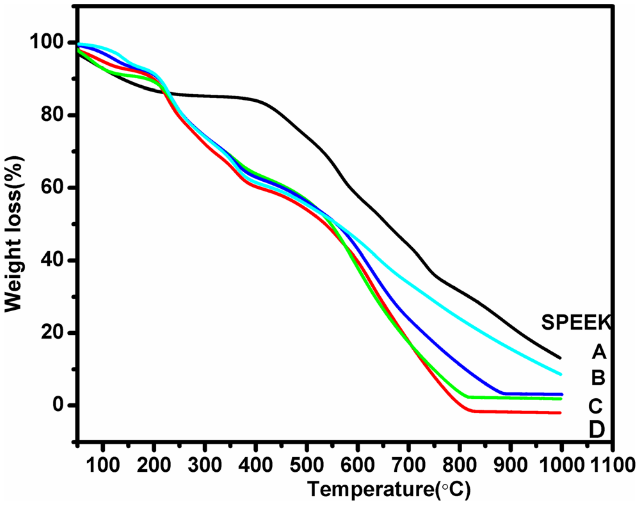


Fig. 8 TGA curve for SPEEK, (A) 98 SPEEK-02 $BaZrO_3$, (B) 96 SPEEK-04 $BaZrO_3$, (C) 94 SPEEK-06 $BaZrO_3$, and (D) 92 SPEEK-08 $BaZrO_3$

SPEEK-$BaZrO_3$ composite membranes occurs predominantly by the Grotthuss mechanism.

Oxidative stability

The oxidative stability is essential for the composite in PEM usage. The chemical stability test was performed in hydrogen peroxide and the observations are shown in Table 3. The oxidative stability of SPEEK and SPEEK-$BaZrO_3$ composite membranes were examined by observing their dissolving characters in Fenton's reagent at 80 °C. From Table 3, the addition of $BaZrO_3$ nanoparticles to the pristine SPEEK membrane decreases its weight residue from 93.50 to 91.81% after Fenton's test. The pristine SPEEK membrane began to break after 72 min. There was no weight loss observed in 92 wt% SPEEK-08 wt% $BaZrO_3$.

Thermogravimetric analysis

Thermal stability is one of the key parameters for the PEM to ensure a long-life guarantee of the PEMFCs. Thermal stability of the prepared polymer composites was analyzed by TGA from 50 to 1000 °C as shown in Fig. 8. The first weight loss occurred at around 100 °C which indicates the adsorbed water at the time of loading sample. The second weight loss region starting from 200 to 250 °C is attributed to the decomposition of sulfonic acid groups of SPEEK [42]. The third weight loss occurred in the region 380–550 °C that corresponds to the melting of the non-polar crystallite back bone of PEEK polymer. However, the presence of the $BaZrO_3$ leads to increase of the decomposition temperature of nanocomposite membranes compared with SPEEK membranes. The perovskite with cubic $BaZrO_3$ is a promising one in HT-PEM fuel cells due to its high melting point (2920 °C). In addition, $BaZrO_3$ has excellent thermal stability and resistance due to a low coefficient of thermal expansion ($\alpha = 87 \times 10^{-7}$/°C between RT and 1080 °C) [43]. The results obtained from the TGA show that 94 wt% SPEEK-06 wt% $BaZrO_3$ polymer composite membrane exhibits excellent thermal stability and is a potential candidate for HT-PEM fuel cell applications with appropriate high conductivity as well as good thermal stability.

Table 3 Oxidative stability for SPEEK and prepared polymer composites

Membranes	Retained weight (%)	Rupture time (min)
SPEEK	93.5	72
98 SPEEK-02 $BaZrO_3$	93.0	65
96 SPEEK-04 $BaZrO_3$	92.1	63
94 SPEEK-06 $BaZrO_3$	91.8	62

Scanning electron microscopy analysis

The surface morphology and dispersion of $BaZrO_3$ nanoparticles in the SPEEK composite membranes were investigated by scanning electron microscopy (SEM) analysis. Figure 9a shows smooth and uniform surface morphology of SPEEK and without any obvious agglomeration that occurred in the polymer matrix. Figure 9b shows the surface image of $BaZrO_3$, and it depicts the crystalline nature and also agrees with XRD [20]. $BaZrO_3$ nanoparticles are uniformly distributed in the system; Fig. 9c–f uniform distributions of $BaZrO_3$ nanoparticles in 94 wt% SPEEK-06 wt% $BaZrO_3$ polymer composite membranes indicate the interaction between SPEEK and $BaZrO_3$ nanoparticle which plays an important role in the proton conductivity. When the amount of $BaZrO_3$ was increased to 8 wt%, there is agglomeration that occurred in the prepared polymer electrolyte system.

Atomic force microscopy surface topography

Surface topography was studied by employing atomic force microscopy (AFM) to explore the topographical characteristics of SPEEK and 94 wt% SPEEK-06 wt% $BaZrO_3$ polymer electrolyte systems. Figure 10(A) shows the three-dimensional smooth surface of SPEEK. Figure 10(B) shows the increase of the number of pores in the proton-conducting polymer electrolyte after incorporating $BaZrO_3$ nanoparticles. The average roughness (R_{rms}) parameter was calculated using the expression

$$R_{\mathrm{rms}} = \left(\frac{1}{N} \sum_{i=1}^{N} |Z_m - Z_i| \right)$$

where N is the number of deviations in height (Z_i) from the profile means value (Z_{m}) [14]. In addition, the rms roughness of the sample has been calculated and it is of the order of

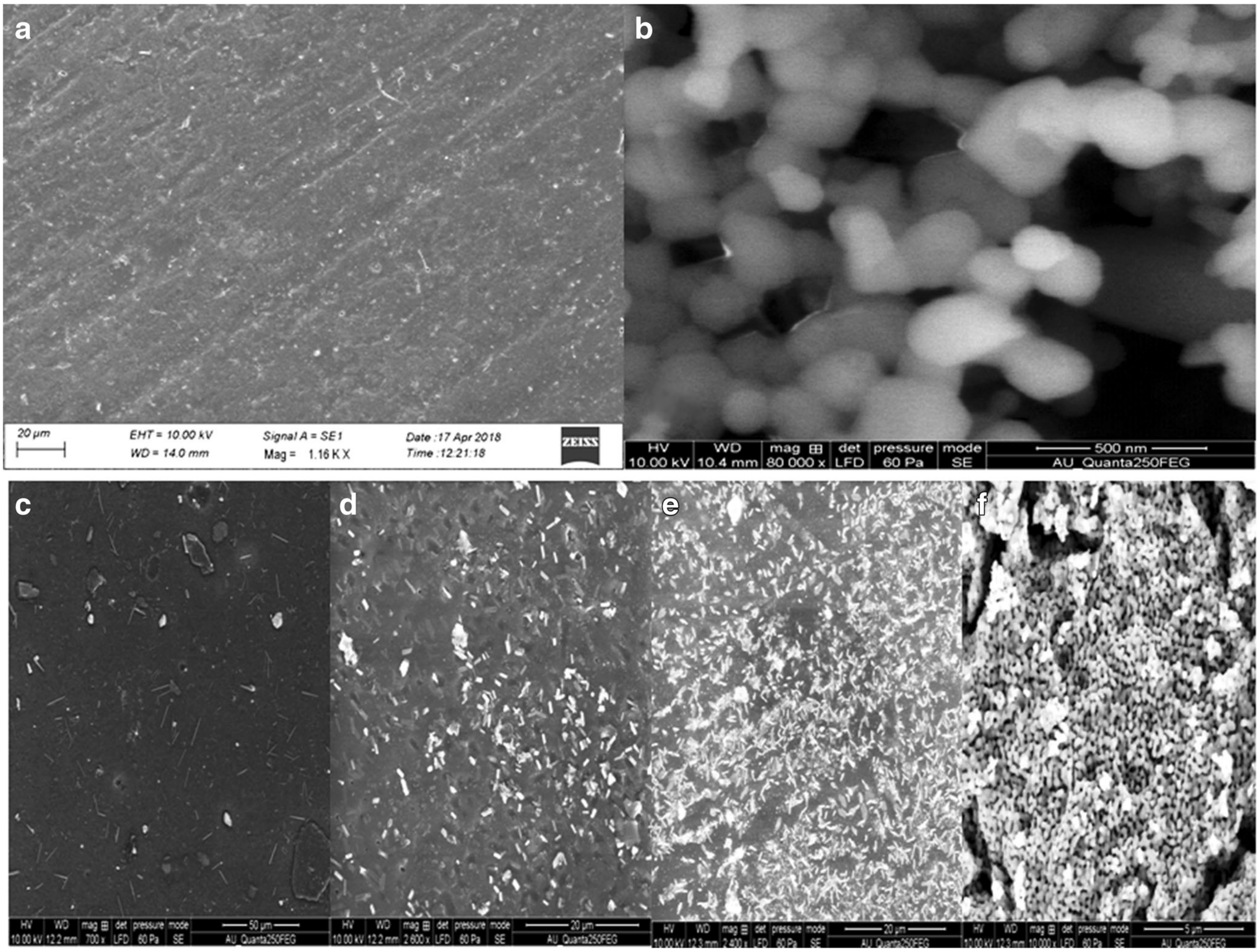


Fig. 9 SEM images for **a** SPEEK, **b** BaZrO3, **c** 98 SPEEK-02 BaZrO3, **d** 96 SPEEK-04 BaZrO$_3$, **e** 94 SPEEK-06 BaZrO$_3$, and **f** 92 SPEEK-08 BaZrO$_3$

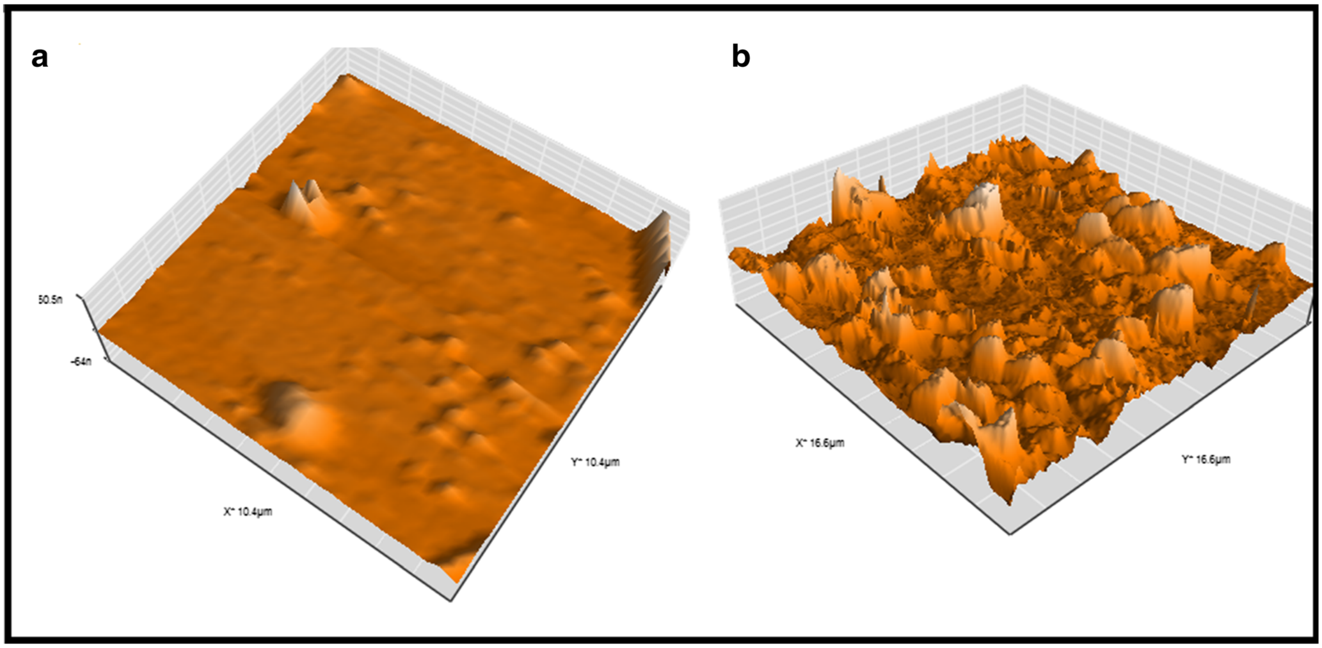


Fig. 10 AFM images for (A) SPEEK and (B) 94 SPEEK-06 BaZrO$_3$

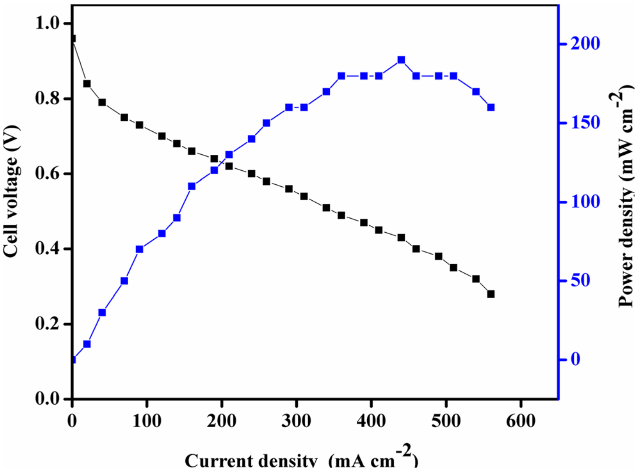


Fig. 11 Polarization curve for 94 SPEEK-06 BaZrO$_3$ at 90 °C

55 nm. Hence, this type of proton-conducting polymer electrolyte can be used in fuel cell application to achieve better proton conductivity which is confirmed by AFM.

Fuel cell performance

94 wt% SPEEK-06 wt% BaZrO$_3$ polymer composite membranes were also used for their fuel cell test in PEMFC in H$_2$/O$_2$ by making membrane electrode assemblies (MEAs). The catalyst loading on both anode and the cathode (active area = 5 cm^2) was kept at 0.5 mg/cm^2. Figure 11 depicts the cell voltage, current density, and power density curve for 94 wt% SPEEK-06 wt% BaZrO$_3$ at 90 °C. The maximum current density of 180 m A cm^{-2} and power density of 153 m W cm^{-2} at a cell voltage of 0.5 V were obtained at 90 °C. The result suggests that 94 wt% SPEEK-06 wt% BaZrO$_3$ composite membrane is a potential candidate for use in PEMFC.

Conclusion

SPEEK-BaZrO$_3$ polymer nanocomposite membranes were prepared by solvent casting technique. The degree of sulfonation of 65% was obtained for the SPEEK through NMR, IEC, and CHNSO studies. The structural functionalities and polymer chain interaction were identified by XRD and FTIR techniques. The composite membranes 94 wt% SPEEK-06 wt% BaZrO$_3$ showed the maximum proton conductivity of 3.12×10^{-1} S/cm at 90 °C. The temperature-dependent proton conductivity of the above system seems to obey Arrhenius behavior and Grotthuss mechanism. The above composite membrane exhibited current density and power density of 280 m A cm^{-2} and 183 m W cm^{-2} respectively. It is concluded that the 94 wt% SPEEK-06 wt% BaZrO$_3$ polymer composite membrane is a potential candidate for PEM fuel cell applications.

Acknowledgements The authors S. Rajendran and K. Selvakumar are thankful to UGC, New Delhi, for the award of Emeritus fellowship and UGC-BSR fellowship, and the corresponding author thanks the DST SERB for funding respectively. The authors thank the Anabond Sainergy Fuel Cell Center, Chennai, for testing the PEMFC.

References

1. Ph.Colomban (1992) Proton conductors: solids, membranes and gels-materials and devices, Cambridge University press 90–95
2. Salarizadeh P, Javanbakht M, Pourmahdian S, Beydaghi H (2016) Influence of amine functionalized iron titanate as filler for improving conductivity and electrochemical properties of SPEEK nano composite membranes. Chem Eng J 299:320–321
3. Liang B, Zhan W, Qi G, Lin S, Nan Q, Liu Y, Cao B, Pan K (2015) High performance graphene oxide/polyacrylonitrile composite pervaporation membranes for desalination applications. J Mater Chem A 3:5140–5147
4. Rajendran S, Kesavan K, Nithya R, Ulaganathan M (2012) Transport, structural and thermal studies on nano composite polymer electrolytes for Li –ion battery applications. Curr Appl Phys 12:789–793
5. Ghalot S, Sharma PP, Kulshrestha V (2015) Dramatic improvement in ionic conductivity of water desalination efficiency of SGO composite membranes. Sep Sci Technol 50:446–453
6. Mayahi N, Ismail AF, IIbeygi H, Othman D, Ghasemi M, Norddin MNAM, Matsuura T (2013) Effect of operating temperature on the behavior of operating temperature on the behavior of promising SPEEK/CSMM electrolyte membrane for DMFCs. Sep Sci Technol 106:72–81
7. Ahmad H, Kamarudin SK, Hasran UA, Daud WRW (2011) A novel hybrid Nafion-PBI-ZP membrane for direct methanol fuel cells. Int J Hydrogen Energy 36:14668–14677
8. Young jung HO, Kim JW (2012) Role of the glass transition temperature of Nafion 117 membrane in the preparation of the membrane electrode assembly in a direct methanol fuel cell (DMFC). IntJHydrogen energy 37:12580–12585
9. Rahimpour A, SiavashMadaeni S, ShahlaG AS, Yaghoub M (2010) The influence of sulfonated polyethersulfone (SPES) on surface nano-morphology and performance of polyethersulfone (PES) membrane. Appl Surf Sci 256:1825–1831
10. Harshad L, VikasKumar AG, Ismail AF (2017) Sulfonated poly(arylene ether sulfone) nanocomposite electrolyte membrane for fuel cell applications: a review sulfonated poly(arylene ether sulfone) nanocomposite electrolyte membrane for fuel cell applications: a review. Int J Hydrogen Energy 452:1063–1074
11. Bai H, Winston Ho WS (2009) New sulfonated polybenzimidazole (SPBI) copolymer-based proton-exchange membranes for fuel cells. J Taiwan Inst Chem Eng 40:260–267
12. Uma T, Parrondo J, Ram babu B (2012) Alternative proton-conducting electrolytes and their electro chemical performance. J Electro Electro Chem 16:2151–2158
13. Vinothkannan M, Kannan R, Kim AR, GnanaKumar G, Nahm KS, Yoo DJ (2016) Facile enhancement in proton conductivity of sulfonated poly(etheretherketone) using functionalized graphene oxide-synthesis, characterization, and application towards proton exchange membrane fuel cells. Colloid Polym Sci 280:389–396
14. Vinothkannan M, Kim AR, GnanaKumar G, Yoon JM, Yoo DJ (2017) Toward improved mechanical strength, oxidative stability and proton conductivity of an aligned quadratic hybrid (SPEEK/FPAPB/Fe$_3$O$_4$-FGO) membrane for application in high temperature and low humidity fuel cells. RSC Adv 7:39034–39048

15. Selva kumar K, Rajendran S, Ramesh Prabhu M (2016) A study of influence on sulfonated TiO_2-poly(vinylidene fluoride-co-hexa fluoro propylene) nano composite membranes for PEM fuel cell application. Appl Surf Sci 418:64–71
16. Gnana kumar G, Kim AR, Nahm KS, Yoo DJ (2011) High proton conductivity and low fuel crossover of Polyvinylidene fluoride – hexafluoro propylene-silica sulfuric acid composite membranes for direct methanol fuel cells. Curr Appl Phys 11:896–902
17. Sgreccia E, Di Vona ML, Knauth P (2011) Hybrid composite membranes based on SPEEK and functionalized PPSU for PEM fuel cells. Int J Hydrog Energy 36:8063–8069
18. Piyush Kumar A, Singh A, Kumar V, Kundu PP (2015) Incorporation of Al_2O_3 within the blend of sulfonated-PVdF-co-HFP and Nafion for high temperature application in DMFCs. RSC Adv 5:63465–63472
19. Hooshyaria K, Javanbakht M, Shabanikia A, Enhessari M (2015) Fabrication BaZrO3/PBI-based nanocomposite as a new proton conducting membrane for high temperature proton exchange membrane fuel cells. J Power Sources 276:62–72
20. Enhessari M, Khanahmadzadeh S, Ozaee K (2010) Structural characterization of BaZrO3 nanopowders prepared by stearic acid gel method. J Iran Chem Res 3:11–15
21. PrabhuNarayanaswamy V, Sangeetha D (2017) Characterization and performance study of phase inversed sulfonated poly ether ether ketone – silico tungstic composite membrane as an electrolyte for microbial fuel cell applications. Renew Energy 102:77–86
22. Attran AM, Javanbakht M, Hooshyari K, Enhessari M (2015) New proton conducting nano composite membranes based on polyvinylalcohol/polyvinylpyrrolidone/$BaZrO_3$ for proton exchange membrane fuel cells. Solid State Ionics 269:98–105
23. Kim AR, Vinothkannan M, Yoo DJ (2018) Sulfonated fluorinated multi-block copolymer hybrid containing sulfonated (poly ether ether ketone) and graphene oxide: a ternary hybrid membrane architecture for electrolyte applications in proton exchange membrane fuel cells. J Energy Chem. https://doi.org/10.1016/j.jechem.2018.02.020
24. Kim AR, Vinothkannan M, Yoo DJ (2017) Sulfonated-fluorinated copolymer blending membranes containing SPEEK for use as the electrolyte in polymer electrolyte fuel cells (PEFC). Int J Hydrog Energy 42:4349–4365
25. Neelakandan S, Kanagaraj P, Sabarathinam RM, Nagendran A (2015) Polypyrrole layered SPEES/TPA proton exchange membrane for direct methanol fuel cells. Appl Surf Sci 359:272–279
26. Muthumeenal A, John Rethinam A, Nagendran A (2016) Sulfonated polyethersulfone based composite membranes containing heteropolyacids laminated with polypyrrole for electrochemical energy conversion devices. Solid State Ionics 296:106–113
27. Javaid zaidi SM (2005) Preparation and characterization of composite membranes using SPEEK-PBI with boron phosphate. Electrochim Acta 50:4771–4777
28. Naresh Muthu R, Rajashabala S, Kannan R (2015) Synthesis and characterization of polymer (sulfonated poly-ether-ether-ketone) based nanocomposite (h-boron nitride) membrane for hydrogen storage. Int J Hydrogen Energy 40:1836–1845
29. Javid zaidi SM (2003) Polymer sulfonation—a versatile route to prepare proton conducting membrane material for advanced technologies. Arab J Sci Eng 28:2B
30. Muthu Lakshmi RTS, Choudhary V, Varma K (2005) Sulphonated poly(ether ether ketone): synthesis and characterisation. J Mater Sci 40:629–636
31. PrabhuNarayanaswamy V, Sangeetha D (2014) Characterization and performance study of sulfonated poly ether ether ketone/ Fe3O4 nano composite membrane as electrolyte for microbial fuel cell. Chem Eng J 243:546–571
32. Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Wang K, Kaliaguine S (2004) Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. J Membr Sci 229:95–106
33. Xie Q, Li Y, Chen X, Hu J, Li L, Li H (2015) Composite proton exchange membranes based on phosphosilicate sol and sulfonated poly(ether ether ketone) for fuel cell applications. J Power Sources 282:489–497
34. Parida S, Rout SK, Caval Cante LS, Sinhaa E, SiuLic M, Subramanian V, Gupta N, Gupta VR, Varela JA, Longo E (2012) Structural refinement, optical and microwave dielectric properties of BaZrO3. Ceram Int 38:2129–2138
35. Yangs T (2008) Preliminary study of SPEEK/PVA blend membranes for DMFC applications. Int J Hydrogen Energy 33:6772–6779
36. Jana KK, Charan C, Shahi VK, Mishra K, Ray B, Rana D, Maiti P (2015) Functionalized poly(vinylidene fluoride) nanohybrid for superior fuel cell membrane. J Membr Sci 481:124–136
37. Bagheri A, Javanbakht M, Beydagi H, Salarizadeh P, Shabanikia A, Amoli HS (2016) Sulfonated poly (ether ether ketone) and sulfonated poly vinylidene fluoride –co-hexa fluoro propylene based blend proton exchange membranes for direct methanol fuel cell applications. RSC Adv 6:39500–39510
38. Zhao L, Li Y, Zhang H, Wu W, Liu J, Wang J (2015) Constructing proton-conductive highways within an ionomer membrane by embedding sulfonated polymer brush modified graphene oxide. J Power Sources 286:445–457
39. de Souza ECC, Muccillo R (2010) Properties and applications of perovskite proton conductors. Mater Res 13:385–394
40. Hooshyari KH, Javanbakht M, Pourmahdian S (2014) Nano composite proton exchange membranes based on Nafion containing Fe_2TiO_5 nano particles in water and alcohol environments for PEMFC. JMembrSci 454:74–81
41. Ishihara T (2009) Perovskite oxide for solid oxide fuel cells. Springer link
42. Onishi T and Helgaker, (2013) A theoretical study on proton conducting mechanism in $BaZrO_3$ Perovskite
43. Vijay sankar R, Savitha T, De N et al (2012) Preparation and characterization of composite membranes based on sulfonated PEEK and AlPO4 for PEMFCs. Solid State Ionics 216:83–89