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Development of proton conductive polymer electrolytes composed of sulfonated poly(ether ether ketone) and Brønsted acidic ionic liquid (1-methylimidazolium tetrafluoroborate)

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ABSTRACT

This article relates to the synthesis, characterization and dielectric measurements of solid polymer electrolytes, derived from the ionic interaction of sulfonated poly(ether ether ketone) (sPEEK) and a Brønsted acidic ionic liquid (1-methylimidazolium tetrafluoroborate, [Hmim][BF_4]) for electrochemical applications. The efficiency of the interaction was examined by incorporating different amounts of ionic liquid (IL) with the sulfonated polymer matrices having three different degrees of sulfonation (DS). The polymer matrices and composite electrolytes were systematically characterized with ^{1}H NMR, FT-IR, SEM, TGA and DMA. Anhydrous proton conductivity and dielectric measurements were studied in detail with varying temperature and frequencies. The presented analyzes revealed that sPEEK$_{1.0}$–2 sample (2.50–3.51 $\times$ 10^{-1} Sm^{-1} at 380–450 K) exhibited maximum proton conductivity and thermomechanical stability under anhydrous environment. Dielectric measurements also provided results confirming proton conductivity measurements. Furthermore, sPEEK$_{1.0}$–2 composite membrane exhibited higher glass transition temperature and reasonable storage modulus value (T_g = 157 °C; E' = 0.22 GPa) compared to IL-doped sPEEK membranes presented in the literature. The work herein opens new prospects for the as-synthesized materials to use as a solid polymer electrolyte for electrochemical applications such as high temperature proton exchange membrane fuel cells (HT-PEMFC) in a wide temperature range.

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1 Introduction

Solid polymer electrolytes (SPEs) play an important role for the development of new energy sources such as fuel cells, sensors, electrochromic systems, lithium polymer batteries and photoelectrochemical solar cells in recent years [1]. In these energy sources, SPEs should be highly ionic conductive under different operating conditions in a wide temperature range. Nafion® is the widely used commercial membrane in proton exchange membrane fuel cells (PEMFCs) due to its high mechanical/chemical stability and high ionic conductivity [2, 3]. Moreover, it enables high cell performance at low temperatures (60–80 °C) when fully saturated in water. On the other hand, disadvantages such as the difficulty of humidity control, the catalyst poisoning and the requirement of high purity hydrogen are encountered under standard cell conditions. Unless optimum humidity of the electrolytes is maintained, low proton conductivity and hence low cell performance will be inevitable [4].

As seen in the example of Nafion®, research has focused on the development of alternative membranes with high ionic conductivity even in anhydrous conditions (above 100 °C) in order to overcome these limitations in electrochemical devices [5–7]. The initial studies for this purpose focused on the modification of currently used commercial membranes with various additives/processes to improve their water retention [8–11]. However, recently many studies have been reported to develop new SPEs which can also maintain high proton conductivity and thermomechanical stability in anhydrous environment. These studies targeting the development of high temperature proton conductive SPEs are mainly based on three main approaches: (i) modification of perfluoro sulfonic acid (PFSA) membranes with organic/inorganic additives [12, 13], (ii) production of sulfonated polyaromatic blend/composite membranes based on poly(ether ether ketone) (PEEK), polysulfone (PS), polybenzimidazole (PBI), etc. [14–17], (iii) production of acid–base interactive polymer electrolytes such as phosphoric acid-doped PBI [18–21].

Ionic liquids (ILs) are ionic salts that have been commonly used for organic synthesis, separation processes, polymerization, and electrochemical applications due to their high boiling temperatures (above 100 °C). In recent years, their superior characteristics such as ionic conductivity and good thermal stability have gained attention to utilize them in electrochemical applications. ILs are structurally inorganic anion-organic cation pairs. ILs containing tetrafluoroborate (BF_4^-), acetate ($A\bar{c}$), hexafluorophosphate (PF_6^-), trifluoromethanesulfonate ($CF_3SO_3^-$) as anion groups can be prepared depending on the desired application while imidazole and pyridine are commonly known cationic groups [22, 23]. In the literature, the performance of ILs in electrochemical devices such as dye sensitive solar cells [24], super capacitors [25], lithium batteries [26], electrochemical sensors [27] and fuel cells [28, 29] has been extensively investigated. Various approaches to the use of ILs for development of polymer electrolytes are also diversified in literature: (i) ILs were used directly as electrolyte [30], (ii) ILs were used as additive to polymer electrolyte backbone [31], (iii) polymer electrolytes were prepared by polymerization of IL-soluble monomers [32] and (iv) polymer electrolytes were prepared by polymerization of polymerizable ILs [33].

Recently, polymeric materials such as poly(arylene ether ketone) (PAEK), polysulfone (PS), polyimide (PI), polybenzimidazole (PBI) and poly(ether ether ketone) (PEEK) have been presented as promising membrane materials for electrochemical applications due to their superior chemical/thermal strength and easy processability. Among aromatic hydrocarbon-based polymer electrolytes, PEEK has been reported as good membrane candidate for electrochemical devices due to its mechanical, chemical and thermal stability [34]. The low ionic conductivity of PEEK in pure form should be improved by various copolymerization processes or functional group additions. Sulfonation and chloromethylation processes are commonly used for the enhancement of ionic conductivity [35–37]. In our previously published work, the effects of degree of sulfonation (DS) on proton conductivity in standard fuel cell applications (60–80 °C) were investigated [38]. In another reported study of our group, dielectric properties and thermomechanical behavior of sPEEK (30%, DS) membranes doped with 1-ethyl-3-methylizdazolium tetrafluoroborate salt were investigated [39].

Herein, sPEEK/IL composite membranes with different DS were prepared as polymer electrolytes with high ionic conductivity and thermal/mechanical stability for electrochemical processes such as HT-PEMFCs. The synthesis was driven by the ionic interaction between the sulfonic acid groups formed in the polymer chain by sulfonation and the imidazole cations of IL (1-methylimidazolium tetrafluoroborate, [Hmim][BF_4]). The composite membranes (sPEEK/[Hmim][BF_4]) were diversified depending on the amount of IL. Sulfonation process was verified by FT-IR and ^{1}H-NMR analysis, and DS of the sPEEK polymer matrices were determined by analytical titration method. The chemical structures of sPEEKs, IL and sPEEK/[Hmim][BF_4] composite membranes were tested by FT-IR analysis. Morphological, thermal and mechanical properties of sPEEKs and composite membranes were investigated by SEM, TGA and DMA, respectively. Water uptake-swelling ratio, proton conductivity (σ), dielectric constant (ε'), imaginary part of dielectric permittivity (ε'') and real part of electric modulus (M') values of composite membranes were determined. The effect of DS and IL addition on the proton conductivity, thermal/mechanical stability and dielectric behavior of polymer electrolytes was discussed in detail.

2 Experimental details

2.1 Materials

Poly(ether ether ketone) (PEEK) was obtained from Röchling Sustaplast SE & Co.Kg. PEEK was dried at 65 °C for 24 h before use. Sulfuric acid (H_2SO_4, 95–97%), sodium hydroxide (NaOH, ACS reagent, $\geq$ 97.0%, pellets) and sodium chloride (NaCl, BioXtra, $\geq$ 99.5%) were purchased from Merck and used as received. 1-methylimidazole ($C_4H_6N_2$, 99%), tetrafluoroboric acid solution (48wt.% in H_2O) and N,N-dimethylformamide (DMF, anhydrous, 99.8%) were also supplied from Aldrich and were not treated.

2.2 Preparation of sulfonated poly(ether ether ketone) (sPEEK)

Sulfonated polymer matrices were synthesized according to the procedure given in our previously published work [38]. Primarily, 1 g of dried PEEK was dissolved in 10 mL of H_2SO_4. The suspension was then sulfonated at 60 °C for 60 min. The resulting solution (a dark red viscous solution) was slowly dropped to a 1 L distilled water/ice mixture to remove the heat and terminate the reaction. The final product was washed with distilled water to pH 5–6 and subsequently dried at 65 °C for 48 h. The resultant sulfonated polymer was coded as sPEEK-1. In order to determine the effect of the sulfonation time, the same procedure was used to sPEEK-2 and sPEEK-3, which were assigned to 120 and 180 min, respectively.

2.3 Preparation of IL (1-methylimidazolium tetrafluoroborate, [Hmim][BF_4])

1-Methylimidazole (7.5 g, 92 mmol) was placed in a cold-water bath (0–2 °C), and tetrafluoroboric acid (12.29 ml, 92 mmol, 50% solution in water) solution was added dropwise (over 30 min) under vigorous stirring. The mixture was then further stirred for 2 h. In the rotary evaporator, the aqueous solution was removed in vacuum (60–70 °C) to obtain the ionic liquid (yield: 98.7%, elemental analyses, wt; theoretical: C%: 32.82, H%: 4.42, N%: 16.31, experimental: C%: 32.73, H%: 4.31, N%: 16.30) [40].

2.4 Preparation of composite membranes (sPEEK$_n$-(1–3))

IL-doped sPEEK composites were prepared with solution casting method. A certain amount of sPEEK was firstly dissolved in DMF, and the solution was stirred for 2 h. The required amount of IL was added to the polymer solution and mixed at room temperature for 4 h. Then, the as-obtained mixtures were poured into glass petri dishes for 48 h at 40 °C to remove solvent. The prepared membrane material was coded sPEEK$_n$- (1–3), where n represents the mole ratio of HSO_3/imidazolium. In this study, two ratios were set as 0.5 and 1. The composition of the as-obtained polymers and composite samples is presented in Table 1.

2.5 Characterizations

The ion exchange capacity (IEC) values of the sulfonated polymer structures to be used as polymer matrices were calculated. For the determination of IEC, 0.1–0.2 g of dried sPEEK samples were left in 50 mL of saturated NaCl solution at 50 °C for 48 h in order to allow the displacement of H^+ and Na^+ ions in the sulfonic acid groups. The solution was then titrated with 0.1 N NaOH to obtain IEC with the following equation:

Table 1 sPEEK matrices and sPEEK/[Hmim][BF_4] composite membranes, sulfonation times and their HSO_3/IL compositions

Sample	t (Sulfonation time, min)	n (mol ratio, HSO_3/IL)
PEEK	–	–
sPEEK-1	60	–
sPEEK-2	120	–
sPEEK-3	180	–
$sPEEK_{0.5}$–1	60	0.5
$sPEEK_{1.0}$–1	60	1.0
$sPEEK_{0.5}$–2	120	0.5
$sPEEK_{1.0}$–2	120	1.0
$sPEEK_{0.5}$–3	180	0.5
$sPEEK_{1.0}$–3	180	1.0

$$\mathrm{IEC} = (V_{\mathrm{NaOH}} \times N_{\mathrm{NaOH}})/W_{\mathrm{p}} \tag{1}$$

(V_{NaOH} = NaOH consumption; N_{NaOH} = NaOH normality; W_{p} = dry weight of membrane or polymer after ion exchange).

Degrees of sulfonation (DS) of the sulfonated polymer matrices were also calculated by using the obtained IEC values by following formula [41]:

$$\mathrm{DS}(\%) = [(288 \times \mathrm{IEC})/(1000 - 103 \times \mathrm{IEC})] \times 100 \tag{2}$$

where 288 g mol^{-1} is the mass of the unit of the initial polymer (PEEK), and 103 g mol^{-1} is the molar mass of the SO_3Na group.

Nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL ECZ500R 500 MHz (11.75 T) instrument at room temperature to verify the sulfonation. For analysis, polymer solution was prepared with deuterated dimethyl sulfoxide (DMSO-d6).

Fourier transform infrared spectroscopy (FT-IR) measurements were used to characterize the prepared IL, sulfonated polymer matrices, and composite polymer electrolytes. The analysis was performed with PerkinElmer Spectrum 100 instrument containing the ATR unit, at a wavelength range of 650–4000 cm^{-1} and at room temperature.

Scanning electron microscopy (SEM) analysis of the solid polymer electrolytes was obtained by Carl Zeiss 300VP system.

Thermogravimetric analysis (TGA) was performed to determine thermal behavior of sPEEK samples and the as-obtained composite membranes. The analysis was carried out with a SEIKO TG/DTA 6300 instrument under nitrogen flow, in the temperature range of 25–800 °C at a heating rate of 10 °C min^{-1}.

Dynamic mechanical analysis (DMA) tests were carried out to examine the mechanical properties of composite proton exchange membranes in a wide range of temperature and frequency ranges. The analysis was performed with the SEIKO DMS 6100 device at a heating rate of 2 °C min^{-1} and in tension mode.

Water uptake (WU) and swelling ratio (SR) of polymer electrolytes were determined by measuring the weight and length differences between the wet and dry membranes. For the WU (%) and SR (%) measurements, polymer electrolytes were fully soaked in the containers filled with distilled water at 80 °C for 24 h. Subsequently, the samples were brought out, the excess water on the surface wiped off and weighed. Then, dry mass was measured after keeping the samples in a vacuum oven for 24 h at 80 °C. WU (%) and SR(%) were calculated by following equations [42]:

$$\mathrm{WU}(\%) = \frac{Wwet - Wdry}{Wdry} \times 100 \tag{3}$$

$$\mathrm{SR}(\%) = \frac{Lwet - Ldry}{Ldry} \times 100 \tag{4}$$

(Wdry = weights of the dry samples; Wwet = weights of the wet samples; Ldry = lengths of the dry samples; Lwet = lengths of the wet samples).

Proton conductivity (σ) and dielectric measurements (dielectric constant (ε'), imaginary part of dielectric permittivity (ε'') and the real part of electric modulus (M')) were carried out using Agilent 4284A LCR Meter system in the frequency range of 40 Hz to 1 MHz and in the temperature range of 300–450 K. Before the measurements, the membrane samples were cut to required dimensions and their surfaces were coated with silver paste to form electrodes. The proton conductivity (σ) values of all membranes prepared in the study were calculated using the following formula:

$$\sigma(S/m) = \omega C_{\mathrm{p}} d(\tan\delta)/A \tag{5}$$

Dielectric parameters (ε', ε'', M') were calculated using following formulas:

$$\varepsilon' = C_{\mathrm{p}} d/\varepsilon_0 A \tag{6}$$

$$\varepsilon'' = \varepsilon' \tan\delta \tag{7}$$

$$M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2) \tag{8}$$

($\omega = 2\pi f$ = angular frequency, where f = frequency; C_P = capacitance of the sample; d = thickness of sample; tan δ = dielectric loss factor; A = effective surface area of sample; ε_0 = dielectric permittivity in vacuum is equal to 8.85×10^{-4} F cm^{-1}).

3 Results and discussion

Sulfonation reactions, which forms sulfonic acid groups in the PEEK polymer backbone, were carried out at different reaction times (60, 120, 180 min) to prepare three different polymer matrices with various DS. The effect of IL amount on proton conductivity, thermal/mechanical and dielectric behavior was investigated by the addition of IL to the sulfonic acid groups in equimolar and doubling (n = 1.0 and 0.5). The basic idea in the use of sPEEK and IL is that the ionic interaction between the sulfonic acid groups in the polymer matrix and the cation group imidazole in the IL structure improves proton conductivity. The ionic interaction between the sulfonic acid groups and imidazole also prevents the migration observed in IL-doped membranes [40]. After the sulfonation processes, IEC values and DS of sPEEK materials were determined by methods mentioned above and relevant results are depicted in Table 2.

As seen in Table 2, the IEC values of sPEEK-1, sPEEK-2 and sPEEK-3 polymer matrices were determined as 1.00, 1.72 and 2.19, respectively, indicating that the capacity enhanced with increasing sulfonation time. The improvement in the IEC values resulted in increasing DS. The highest DS (81.44%) was achieved with the three-hour sulfonation process. That is to say, the amount of the sulfonic acid groups attached on PEEK backbone increased with longer reaction time [38]. The physicochemical properties and proton conductivity of sPEEK polymer matrices significantly depend on DS. The high DS enables high proton conductivity due to the density of sulfonic acid groups in the polymer backbone. However, on the contrary, the high DS lowers the mechanical strength and stiffness. The density of sulfonic acid groups in highly sulfonated polymer matrices can lead to clusters and agglomerations. In this case, the density of the sulfonic acid groups and the presence of agglomerated ionomers increase the water uptake capacity of the membranes and hence the swelling capacity. In particular, mechanical strength weakens when the membrane absorbs more water. Therefore, it is important to maintain the mechanical strength as much as possible while improving the proton conductivity with increasing DS. As mentioned before, the main approaches to achieving this optimization are to create composite structures with various inorganic additives and blending with basic polymers [35, 43].

3.1 ^{1}H nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR measurement was performed to verify the sulfonation process. Figure 1a−c presents the ^{1}H NMR spectrum of the sPEEK-2 polymer matrix, resonance ranges of all H-protons and their schematic representation.

As seen in Fig. 1c, there are nine electromagnetically different types of hydrogen in the sPEEK structure. H-a, H-b, H-c represent the aromatic hydrogens in each PEEK repeating unit. While the sPEEK unit has the characteristic acidic hydrogen attached to the sulfonic acid group, protons of H-a′, H-b′, H-c′, H–d and H-e are also attributed to aromatic hydrogens. The peak of proton H-c in the PEEK repeating unit is at 7.22 ppm (Fig. 1b). The addition of electron-attracting sulfonic acid groups to the structure by the sulfonation process deshielded H-e. In this way, proton H-e is represented at 7.44 ppm with a 0.22 ppm shift compared to the H-c in the PEEK unit. Since H-e is not affected by other hydrogens in

Table 2 Ion exchange capacity (IEC) and degree of sulfonation (DS) values of sPEEK samples [38]

Sample	t (sulfonation time, min)	IEC (ion exchange capacity, meq/g)	DS (degree of sulfonation, %)
PEEK	–	–	–
sPEEK-1	60	1.00	32.10
sPEEK-2	120	1.72	60.20
sPEEK-3	180	2.19	81.44

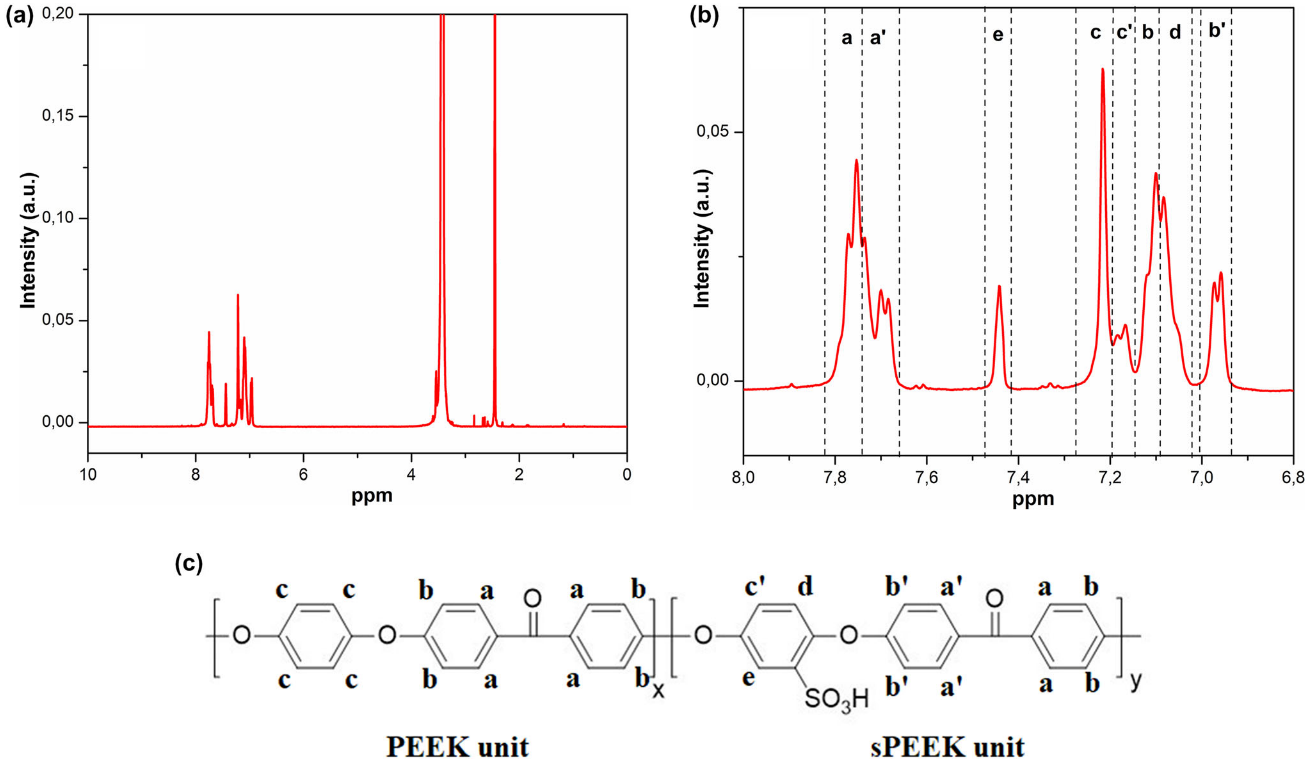

Fig. 1 **a** ^{1}H NMR spectrum, **b** resonance of H-protons, **c** schematic chemical structure of sPEEK-2

sPEEK structure, the peak at 7.44 ppm attributed to H-e is the characteristic peak of the sulfonation process [44].

3.2 Fourier transform infrared spectroscopy (FT-IR)

In order to confirm the chemical structures and functional groups of the as-obtained sPEEK, IL and sPEEK/IL composites, the samples were characterized by FT-IR spectroscopy and the spectrums are illustrated in Fig. 2a, b.

Figure 2a confirms the presence of sulfonic acid groups in the sulfonated polymer matrix and thus the success of sulfonation process. The wide peaks of sPEEK materials at 3400 cm^{-1} corresponded to the vibrations of O–H groups. This broad band of the sPEEK polymer matrix at 3400 cm^{-1} could be assigned to O–H vibration from sulfonic acid groups interacting with molecular water. The peaks observed at 1020 and 1312 cm^{-1} reflected the presence of S–O bonds. Besides, the signals at 1080 and 1218 cm^{-1} demonstrated the presence of S=O and O=S=O bonds, respectively. Additionally, the vibrations detected at 1640 cm^{-1} were attributed to the carbonyl groups present in all samples [45]. The active groups of the as-synthesized IL sample are depicted in Fig. 2b. The highest intensity was observed at 1048 cm^{-1}, indicating the stretching vibration of BF_4^- anion in IL structure. The peak at 840 cm^{-1} was assigned to the C–N stretching. Moreover, the peaks occurred at 2957 and 2880 cm^{-1} were attributed to the symmetric and asymmetric stresses of CH_3, respectively. The characteristic peaks of C=N and C=C stretching modes were observed at 1590 and 1633 cm^{-1}, respectively. In addition, the peaks attributed to C–H plane bending and symmetric C–H stretching vibrations occurred at 760 cm^{-1} and 3156 cm^{-1} [46, 47]. Then, as mentioned above sPEEK/[Hmim][BF_4] composite membranes of each polymer matrix were produced with different mole ratios of HSO_3/imidazole ($n = 0.5$ and $n = 1.0$) depending on the purpose of the study. The formation of sPEEK/IL composite membrane was controlled with the FT-IR spectrum of $sPEEK_{1.0}$–1 given in Fig. 2a. The peak at 3150 cm^{-1} was attributed to the amide groups of the imidazolium. Furthermore, the peak at about 2980 cm^{-1} indicated the presence of aliphatic methyl vibration of the [Hmim][BF_4]. The vibration at 1064 cm^{-1} evidenced the presence of the anion groups of IL (BF_4^-).

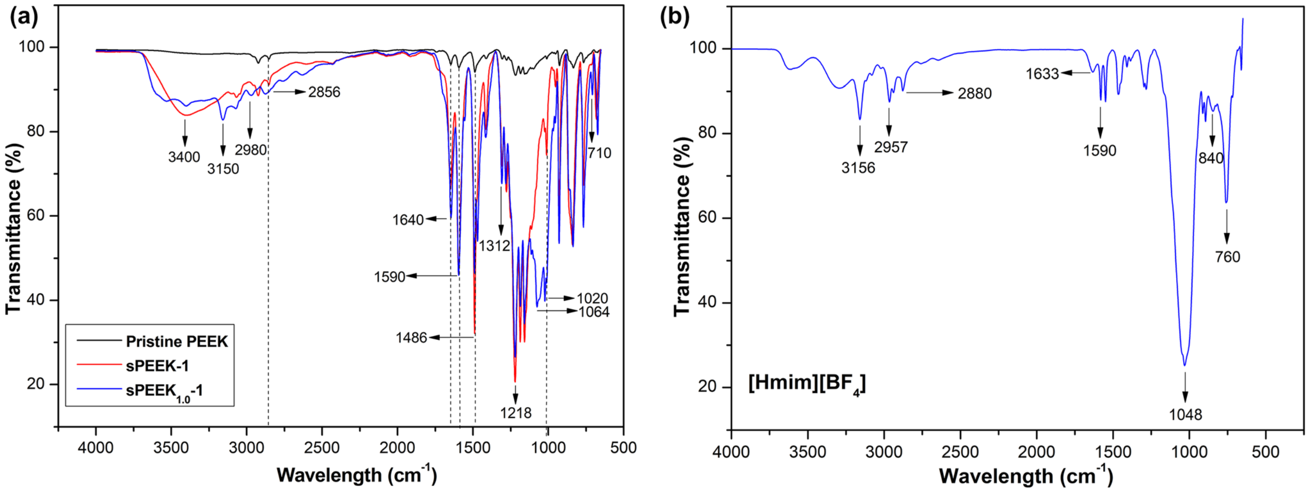

Fig. 2 **a** FT-IR spectra of pure PEEK, sPEEK-1 and sPEEK/IL composite (sPEEK$_{1.0}$–1) samples, **b** FT-IR spectrum of [Hmim][BF$_4$].

Additionally, the absorption bands at 1486, 1590 and 1640 cm^{-1} showed the presence of aromatic rings in the sPEEK matrix. Structural characterizations showed that sPEEK polymer matrices, IL, and sPEEK/[Hmim][BF$_4$] were successfully synthesized in the present study.

3.3 Scanning electron microscopy (SEM)

The morphological structures of sulfonated polymer matrix and composite polymer electrolytes were performed by SEM analysis. In Fig. 3a–c, cross-sectional micrographs of the sPEEK-2 polymer matrix and composite membranes prepared by sPEEK-2 (sPEEK$_{1.0}$–2 and sPEEK$_{0.5}$–2) are presented.

As seen from Fig. 3a, the honeycomb micro-voids were formed in the membrane cross section with sulfonic acid groups formed in the pure PEEK backbone with the sulfonation process. Chain mobility in the polymer backbone increases as the IL contribution increases (Fig. 3b, c). Branched structures are more concentrated in IL-doped polymer electrolytes compared to sulfonated polymer matrix. This functional mobility also enabled the IL-doped membranes to be more flexible, soft and mobile. In addition to sulfonation, these increasing branching and mobility increase the distance between polymer chains, and thus the ionic conductivity.

3.4 Thermogravimetric analysis (TGA)

One of the important criteria for polymeric membranes used in electrochemical systems is thermal stability. In addition, composite polymer electrolytes prepared in the present study are expected to have high thermal resistance at high temperatures and anhydrous environment (above 100 °C). TGA measurements of sPEEK polymer matrices and sPEEK/[Hmim][BF$_4$] composite membranes were performed in the temperature range of 25–800 °C under nitrogen atmosphere. TGA curves of PEEK and representative sPEEK-2 membrane series are presented in Fig. 4. TGA results for all membrane series are also shown in Table 3.

As shown in Fig. 4, the pristine PEEK membrane showed the single polymer main chain degradation, while the sulfonated membrane showed three degradation steps. In terms of the pure PEEK, the only thermal decomposition phase starting at 550 °C was attributed to the degradation of the polymer master chain. In case of the sulfonated PEEK products, the initial weight loss was observed at about 100 °C due to the evaporation of adsorbed moisture in the polymer. The second weight loss zone of sPEEKs occurred in the temperature range of 150–250 °C corresponding to the degradation of the sulfonic acid groups in the composite membrane structure. Moreover, the third weight loss starting at 450 °C was assigned to the degradation of PEEK polymer main chain [48, 49]. Obviously, more than one degradation step was observed for all sPEEK/[Hmim][BF$_4$] composite membranes like the sulfonated polymer matrices. Similarly, the first degradation step starting at around 100 °C could be attributed to the deterioration of the moisture trapped on the membrane structures. Degradation steps starting at ~ 200 °C

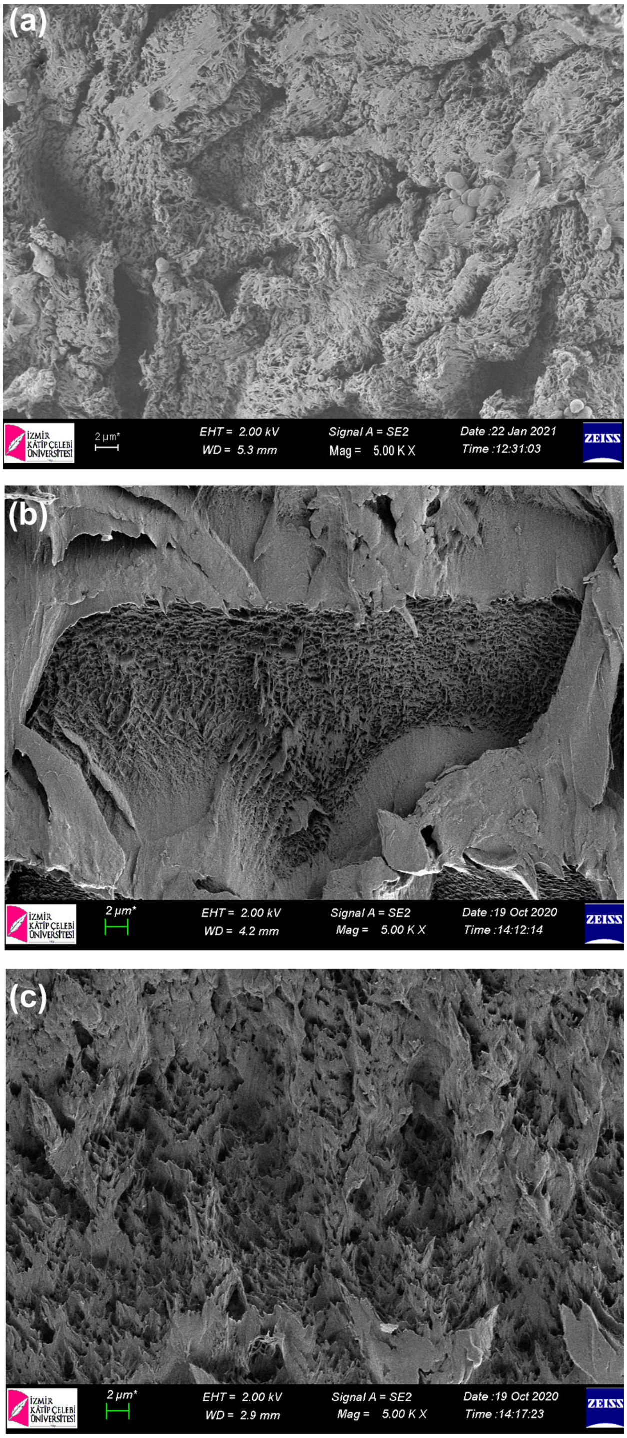

Fig. 3 SEM micrographs of **a** sPEEK-2, **b** sPEEK$_{1.0}$–2 and **c** SPEEK$_{0.5}$–2

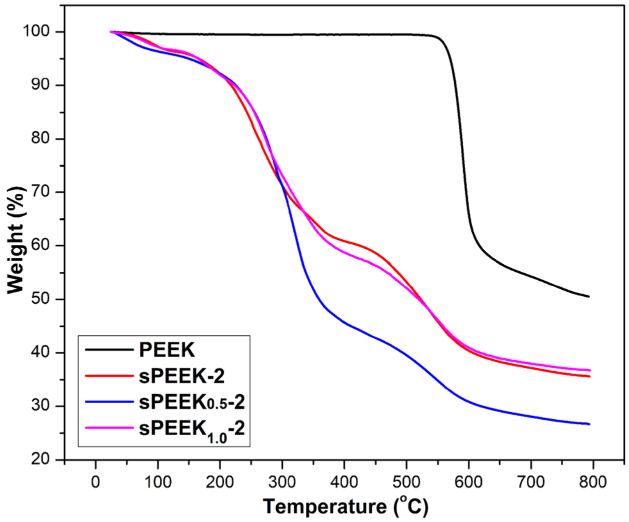

Fig. 4 TGA patterns of pure PEEK and sPEEK-2 membrane series

Table 3 Thermal degradation values of pure PEEK, sPEEK polymer matrices and sPEEK/[Hmim][BF$_4$] composite membranes

Sample	T$_{10}$ (°C)	T$_{50}$ (°C)
PEEK	578.4	790.3
sPEEK-1	228.2	575.9
sPEEK-2	215.9	524.4
sPEEK-3	215.8	541.4
sPEEK$_{0.5}$–1	238.9	552.6
sPEEK$_{1.0}$–1	240.3	556.8
sPEEK$_{0.5}$–2	225	359.3
sPEEK$_{1.0}$–2	223.1	519.9
sPEEK$_{0.5}$–3	204.7	355.8
sPEEK$_{1.0}$–3	187.6	419.2

T$_{10}$ the temperature where 10wt% weight loss has occurred, *T$_{50}$* the temperature where 50wt% weight loss has occurred

were attributed to sulfonic acid groups in composite membrane structures. Furthermore, the thermal stabilities of IL-doped composite membranes prepared with sPEEK-1 product (sPEEK$_{0.5}$ -1 and sPEEK$_{1.0}$-1), which have the lowest DS values, were higher than that of other membranes. It can be therefore indicated that the increasing DS reduced the thermal resistance of the membranes. Regarding the effect of IL amounts, it was observed that the addition of the excess amount IL decreased the thermal strength. This could be due to the IL residues which remained without binding to the sulfonic acid groups in composite membrane structures.

As seen from Table 3, 50% weight loss of the pure polymer was observed at about 800 °C. As DS increased, the weight loss carried out at lower temperature values. The weight losses of 10% were recorded in the temperature range of 215–230 °C, while the weight losses of 50% were observed in the 525–580 °C temperature range for sPEEKs. As the DS increased in IL-doped composite membranes, thermal strength limited depending on the density of sulfonic acid groups in the structure. It was observed that the excess IL (n = 0.5) significantly decreased the thermal resistance, and 50% weight loss was observed at 356 °C for IL-doped composite membranes, having the highest DS (sPEEK$_{0.5}$-3). Similarly, the composite membrane (sPEEK$_{1.0}$-2) consisting of sPEEK and an equimolar IL with a DS of 60.20% had a 50% weight loss at 520 °C, while the sample with an excess IL (sPEEK$_{0.5}$-2) had a 50% weight loss at 360 °C. In the case of thermal endurance, this negative effect observed with an increase in the DS and the IL amount was not significant when considering the high temperature applications. All membranes showed sufficient thermal stability for electrochemical systems such as HT-PEMFC operation (100–180 °C).

3.5 Water uptake (%) and swelling ratio (%) tests

Water uptake plays an important role in proton conductivity as it facilitates the proton mobility in an aqueous environment. The number of acid groups in the membrane and their dissociation ability in water determine the conductivity behavior. As mentioned before, excessive water uptake improves proton mobility but negatively affects mechanical and dimensional stability. The water uptake and swelling ratios of sPEEK polymer matrices and sPEEK/[Hmim][BF$_4$] composite membranes are presented in Fig. 5 and Table 4.

As seen in Fig. 5 and Table 4, the water uptake capacities of sPEEK-(1–2–3) polymer matrices are 16.3, 47.6 and 76.3%, respectively. Additionally, swelling ratios are determined as 5.7, 17.1 and 26.9%. As expected, the water uptake capacities increased due to the increasing DS and acidic group density. On the other hand, with the addition of IL, the water uptake capacity and swelling ratio of each membrane series reduced. In addition, it is seen that this decrease is much more acute in polymer electrolytes with excess IL (n = 0.5). This decrease can be explained by the increase in the hydrogen bonds formation between the sulfonic acid groups and imidazole rings. Hydrogen bonds formation increases the cross-linking in composite membranes. In this way, water absorption is also reduced due to the reduced pore size and pore number. This reduction confirms the strong interaction between the sulfonic acid groups and the imidazole ring, improving the mechanical stability of the membrane by preventing excessive swelling in the aqueous medium in electrochemical applications.

3.6 Proton conductivity tests

Proton conductivities of sPEEK and sPEEK/[Hmim][BF$_4$] composite membranes are presented in Fig. 6. In terms of sPEEK, it was indicated that the increasing DS improved the proton conductivity. This behavior showed that sulfonic acid groups formed in the membrane structure by sulfonation processes contributed to proton jumping zones

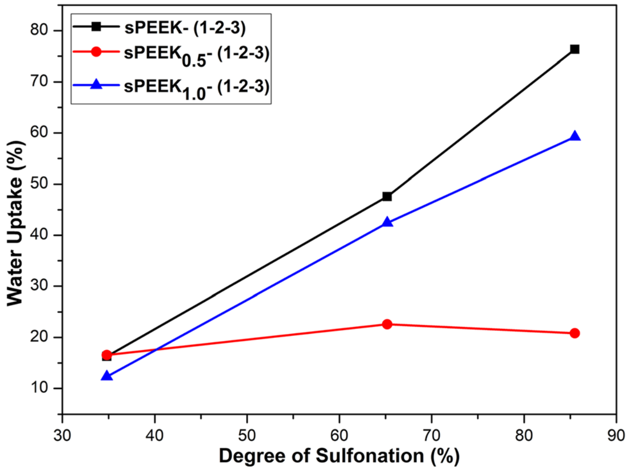

Fig. 5 Water uptake capacities of polymer electrolytes

Table 4 Water uptake (%) and swelling ratio (%) of sPEEK polymer matrices and sPEEK/[Hmim][BF$_4$] composite membranes at 80 °C

Sample	Water uptake (%)	Swelling ratio (%)
sPEEK-1	16.3	5.7
sPEEK-2	47.6	17.1
sPEEK-3	76.3	26.9
sPEEK$_{0.5}$-1	16.1	5.1
sPEEK$_{1.0}$-1	12.3	3.3
sPEEK$_{0.5}$-2	22.6	8.6
sPEEK$_{1.0}$-2	42.4	14.7
sPEEK$_{0.5}$-3	20.8	9.4
sPEEK$_{1.0}$-3	59.2	19.6

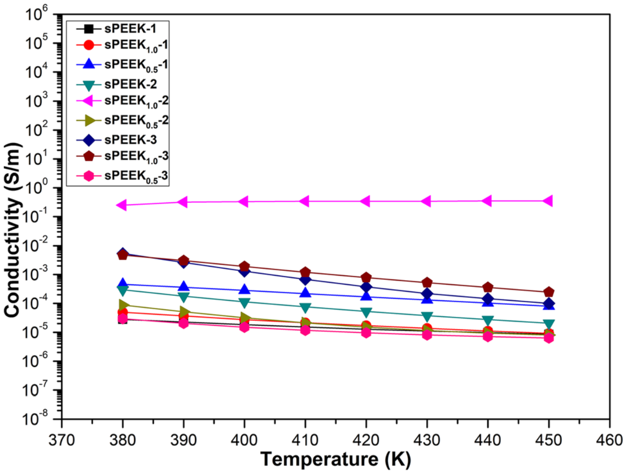

Fig. 6 Proton conductivities of sPEEK and sPEEK/[Hmim][BF_4] samples (1 MHz)

[36, 50]. For sPEEK/[Hmim][BF_4] composites, it could be said that the addition of IL increased proton transfer, resulting higher conductivity. The motivation of the addition of IL to sPEEK matrices was to increase the ionic conductivity of the membranes at high temperature under anhydrous conditions. IL was expected to behave as proton carrier media in the membrane instead of water in proton conductive membranes operated below 100 °C. That is, the addition of IL could provide proton jump zones leading to higher conductivity.

However, it was seen that the conductivity decreased when excess IL was used ($n = 0.5$), and the conductivity values were improved in products where imidazole was taken as equimolar to sulfonic acid at line with the studies [40, 51]. It was observed that IL-doped membrane prepared with sPEEK-2 showed higher conductivity values than that of IL-doped composite membranes prepared with sPEEK-1 and sPEEK-3 polymer matrices. $sPEEK_{1.0}$–2 sample showed almost unchanged conductivity values (2.50×10^{-1} Sm^{-1}–3.51×10^{-1} Sm^{-1}) at high temperatures, while surprisingly the conductivity decreased in all other samples. As stated in the literature, DS has a superior effect over temperature on sPEEK conductivity. Herein, sPEEK membranes having a DS of around 40% did not show any conductivity development by increasing the operating temperature, but rather decreased. Some examples showed that the conductivity of a sPEEK with DS (48%) could increase up to 85 °C and then sharply fell to very low values. In the meantime, for a DS about 70–75%, the sPEEK membrane showed an increase in conductivity and it was indicated to decrease gradually only was observed in anhydrous conditions [35, 52]. With the addition of equimolar IL to the sulfonic acid groups of sPEEK-1 membrane matrix ($sPEEK_{1.0}$–1), the conductivity was increased, and higher values were observed in the excess IL addition ($sPEEK_{0.5}$–1). These results are compatible with the motivation of the work. With the addition of equimolar IL in the sPEEK-2 membrane matrix ($sPEEK_{1.0}$–2), the conductivity increased and displayed the highest conductivity values among all samples. In the case of IL excess ($sPEEK_{0.5}$–2), the conductivity was even lower than the membrane without IL (sPEEK-2). A similar trend was observed in the samples with the highest DS (sPEEK-3). The decrease in conductivity of sPEEK-2 and sPEEK-3 samples with the excess amount of IL could be attributed to the self-condensation of the IL anion in the membrane matrix [53]. In the present study, conductivity values of composite membrane prepared with DS of 60.20% were acceptable for electrochemical applications (3.40×10^{-1} Sm^{-1}–3.51×10^{-1} Sm^{-1}, at the temperature range of 420–450 K).

The temperature dependence of proton conductivities for anhydrous sPEEK and sPEEK/[Hmim][BF_4] composite membranes is shown in Fig. 7. The dc conductivity (σ_{dc}) of the samples was obtained from the plateaus of log σ_{dc} versus log F by linear fitting.

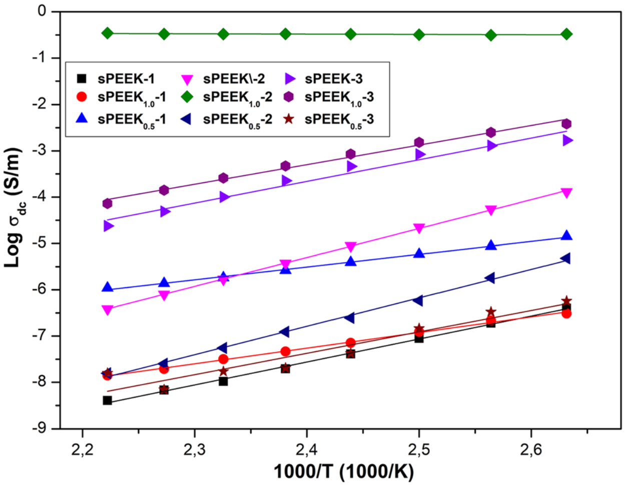

Fig. 7 Temperature dependency of the dc conductivity of sPEEK polymer matrices and sPEEK/[Hmim][BF_4] composite membranes

The conductivity curves demonstrate that the dc conductivity strongly depends on the DS and IL content as well as the temperature. It is clear that the conductivity increases with DS. In this system, the proton conductivity is achieved through sulfonic acid groups and IL molecules. The temperature-dependent behavior of conductivity in polymer electrolytes is generally indicative of a particular conduction mechanism. The composite membranes exhibited Arrhenius behavior, which may be due to the restriction of segmental movements as sulfonic acid groups lead to formation of cross-linking structures to a certain extent at high temperatures [54]. The curves can be fitted by Arrhenius equation:

$$\log \sigma = \log \sigma_0 - \frac{E_a}{RT} \tag{9}$$

(E_a = activation energy for ionic conduction energy (kJ mol^{-1}); σ = conductivity (S m^{-1}); σ_o = pre-exponential factor; T = absolute temperature (K) and R = universal gas constant (8.314 J mol^{-1} K^{-1})).

The activation energy or minimum energy required for proton transfer is attained from the slope of the linear fit, and accordingly the calculated activation energies of sPEEK-(1–3) polymer matrices are 41.29, 28.09, and 22.94 kJ mol^{-1}, respectively. Observing such low activation energy especially for sPEEK$_{1.0}$–2 (0.53 kJ mol^{-1}) may be the reason for the high proton conductivity. The proton transport mechanism under anhydrous conditions can be primarily described by a Grotthuss-type diffusion mechanism. In this mechanism, the proton transport occurs by the hopping of protons over formation of hydrogen bonding between SO_3^- units as well as IL. However, vehicle mechanism may also take place with the increase in IL where the protons travel through the material on a neutral or charged “vehicle” [55]. The decrease in conductivity with the excess amount of IL could be attributed to the self-condensation of the IL anion and increase in ionic-ionic interaction between SO_3^- units and IL in the membrane matrix resulting a cross-linking like structure [56, 57]. An inverse correlation with temperature may be described as limiting the movement of the polymer chains due to evaporation of trapped water and cross-linking to some extent with temperature rise leading to high immobilization of ions [39].

3.7 Dielectric measurements

Dielectric measurements provide elucidation of phase transitions and ion transport mechanisms in polymer electrolytes. Dielectric parameters were evaluated for the membrane series containing sPEEK$_{1.0}$–2 polymer electrolyte, which shows the highest conductivity in proton conductivity measurements. The dielectric constant (ε') curves of the related series are shown in Fig. 8a–c as a function of frequency at varying temperatures (300–440 K).

As seen from Fig. 8a–c, higher ε' values were observed at low frequencies for all samples. As known, dipoles need much more time to orient themselves into the external electric field and high ε' values at low frequency confirm this judgment. The dielectric values decreased sharply with increasing frequency and also showed slight decreases in the higher temperature range. The temperature effect on ε' can be explained by the rearrangement of the sulfonic acid groups with increasing temperature. These reductions could be explained by the evaporation of molecular water attached to the sulfonic acid groups in the membrane structure and the restriction of the polymer chain movement by cross-linking by sulfonation process. It can also be concluded that decreases in dielectric constant with increasing temperature are relatively less effective in applying external electric field at higher frequency [58, 59]. On the other hand, sPEEK$_{1.0}$-2 membrane has higher ε' values compared to other samples. When the amount of IL was equimolar to the sulfonic acid groups in the polymer structure, the plasticizing effect of the IL facilitated the orientation of the electric dipoles and consequently increased the dielectric constant values. The lowest ε' values were seen in sPEEK$_{0.5}$-2 sample. This result can be explained by the fact that the excess IL remaining unbound to the sulfonic acid groups disrupts the dipole orientation [39, 58].

In Fig. 9a–c, imaginary part of dielectric permittivity (ε'') curves for sPEEK-2 membrane series is presented at the same temperature and frequency range.

As seen, ε'' values showed a linear decrease with frequency at almost all temperatures for all membranes. This indicates that the ion transmission mechanism is dependent on both temperature and the nature of restructuring due to structural diffusion [39, 60]. Additionally, capacitive response of IL-doped composite electrolytes exhibits temperature

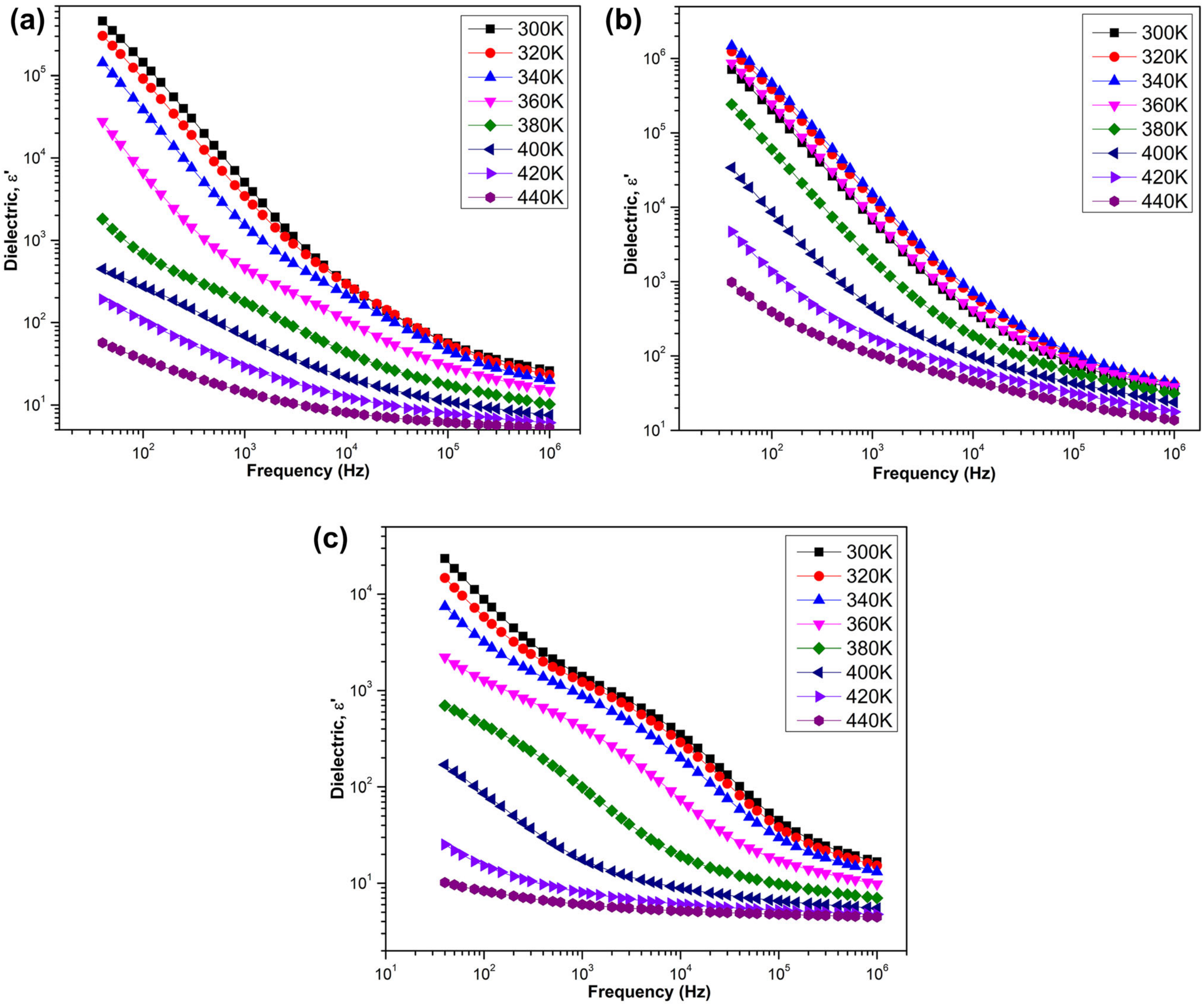

Fig. 8 The variation of dielectric constant (ε′) at varying temperature (300−440 K) and frequency (40 Hz-1 MHz) **a** sPEEK-2, **b** sPEEK$_{1.0}$–2, **c** sPEEK$_{0.5}$–2

dependency rather than restructuring of sulfonic acid active groups. Similar to the dielectric constant (ε′) values, sPEEK$_{1.0}$–2 sample showed the highest ε″ value, while this value is minimum when excess IL is used. The dissociation energy of intermolecular forces such as dipolar forces and hydrogen bonding is lower compared to primary forces such as ionic or covalent bonding. In this way, additives such as salt and IL significantly restrict the segmental movement of the polymer matrix [60]. Excess IL forms a structure that remains unbound to sulfonic acid groups. Therefore, a double layer capacitance can develop due to the ion transfer accumulated between the membrane and the electrodes. At the same time, with increasing frequency, the available drift time decreases and both the real and imaginary parts of the dielectric constant decrease [60, 61].

The frequency dependence of the real part of electric modulus (*M*′) at varying temperatures for sPEEK-2 membrane series is depicted in Fig. 10a-c.

The real part of electrical modulus (*M*′) values increased with increasing frequency in all membranes and all temperature values. Higher *M*′ values seen at high frequencies are attributed to the bulk effect [62]. The fact, that the electric modulus values at lower frequencies are nearly zero, proves that the electrode polarization is at negligible levels [60–62]. The presence of the long tail in the wide frequency range in the low frequency region can be attributed to the large capacitance associated with the electrodes,

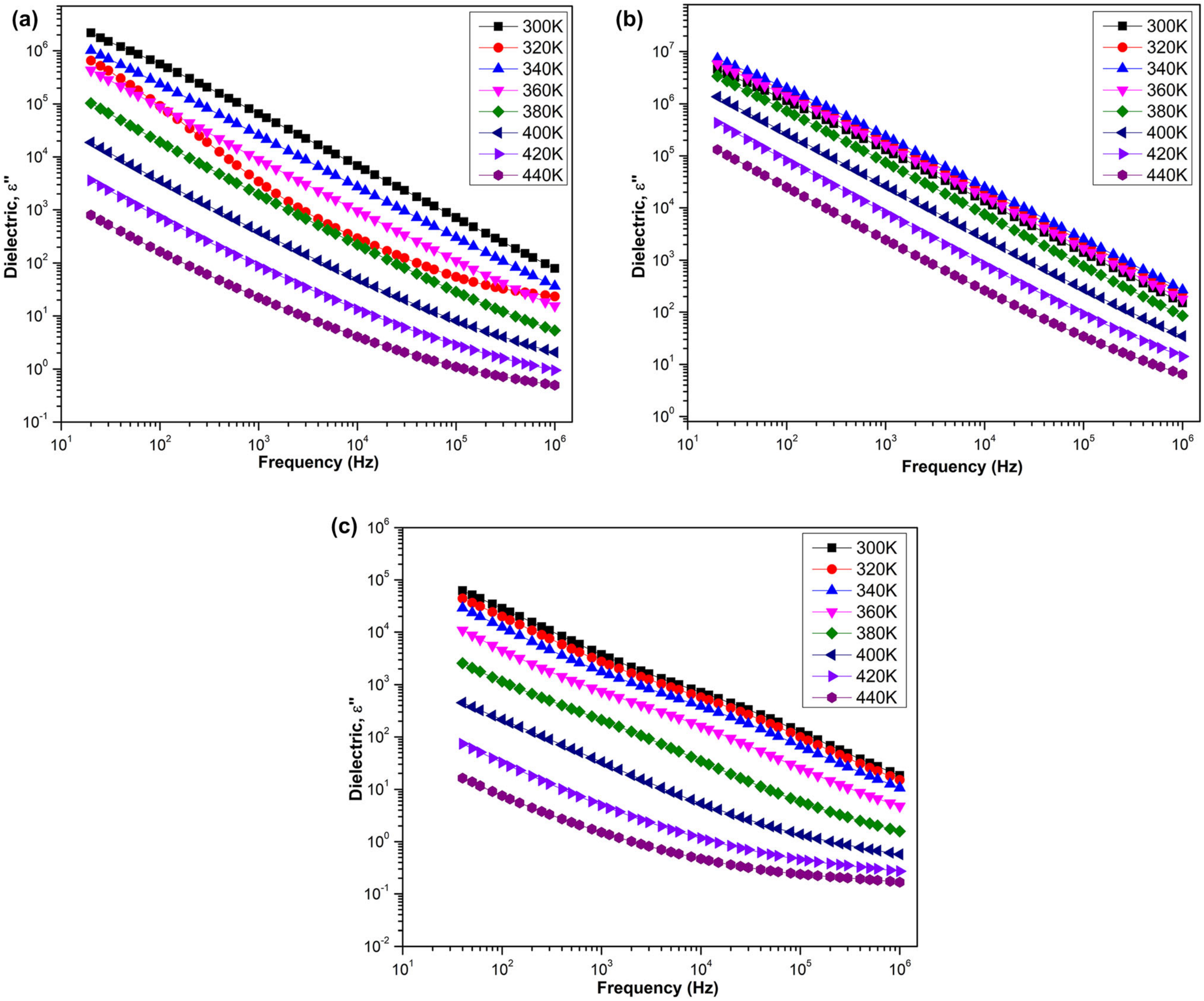

Fig. 9 The variation of imaginary part of dielectric permittivity (ε'') at varying temperature (300–440 K) and frequency (40 Hz-1 MHz) **a** sPEEK-2, **b** sPEEK$_{1.0}$–2, **c** sPEEK$_{0.5}$–2

confirming the non-Debye behavior. In other membranes, electrode polarization is negligible at low temperatures. As temperature increases, electrode polarization becomes more effective and modulus values increase sharply at low frequency values. Low M' values in low frequency regions facilitate ion conduction [62]. The electrical modulus behavior of sPEEK$_{1.0}$–2 membrane is also compatible with high proton conductivity values.

3.8 Dynamic mechanic analysis (DMA)

The mechanical properties of sPEEK and sPEEK/[Hmim][BF$_4$] composite membranes were investigated by DMA. SPEs used in electrochemical processes are expected to exhibit good mechanical strength with high proton conductivity and thermal stability [39, 63]. For this purpose, the storage (E') and loss (E'') modulus of sPEEK-2 and sPEEK$_{1.0}$-2 composite membranes were analyzed, and the DMA plots are given in Fig. 11.

As shown in Fig. 11, the storage (E') and loss (E'') modulus values of the sPEEK membrane were higher compared to IL-doped composite membrane. This result could be due to the plasticizing effect of the presence of IL in the composite membrane structure. The IL could facilitate the chain segment movements of the polymer by reducing the viscosity of the composite membrane [39, 64]. The storage moduli of sPEEK-2 and sPEEK$_{1.0}$–2 composite membranes were

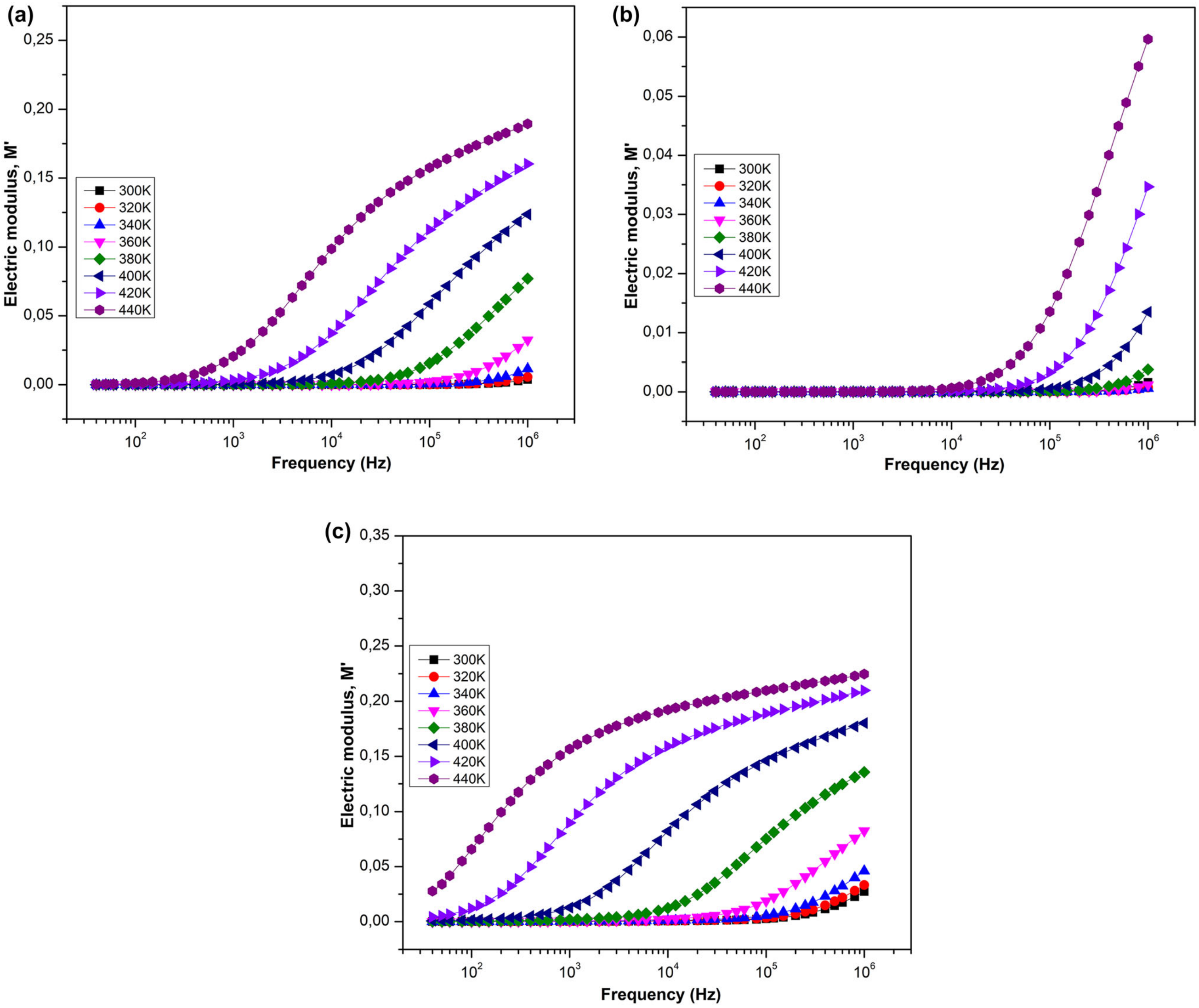

Fig. 10 The variation of electric modulus (M') at varying temperature (300–440 K) and frequency (40 Hz–1 MHz) **a** sPEEK-2, **b** sPEEK$_{1.0}$-2, **c** sPEEK$_{0.5}$-2

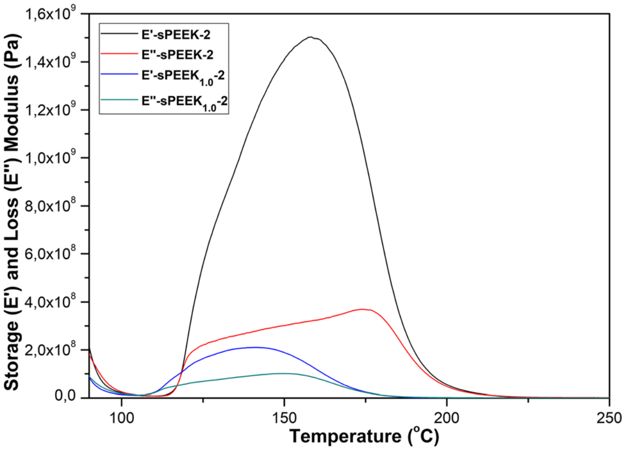

Fig. 11 DMA graphs of sPEEK-2 and sPEEK$_{1.0}$–2 samples

found to be 1.50 GPa and 0.22 GPa, respectively. These maximum stress values are similar to those given in the literature with trifluoromethanesulfonate-based IL-doped sPEEK membranes (2220.5 and 53.92 MPa for sPEEK and sPEEK/IL, respectively) [51]. When the sulfonated polymers and IL-doped sulfonated polymers presented in the literature were considered, it could be said that the sPEEK-2 and sPEEK$_{1.0}$-2 products had reasonable maximum stress at high temperature values [64].

In Fig. 12, changes in tan δ values of sPEEK-2 and sPEEK$_{1.0}$-2 composite membranes were illustrated depending on temperature. From the tanδ graph, it is possible to determine the glass transition temperatures (T_g) of the products depending on the

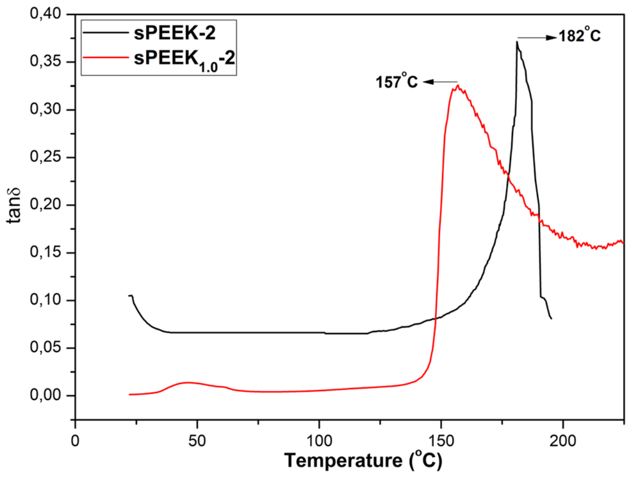

Fig. 12 tan δ graphs of sPEEK-2 and sPEEK$_{1.0}$-2 samples

temperature values at which maximum tanδ values are observed. Considering the statement, it was presented that T_g of the sPEEK-2 membrane was 182 °C while the sPEEK$_{1.0}$-2 composite membrane had a decreased T_g value of 157 °C with the addition of IL. Similar behavior was seen in the storage modulus trend. This behavior could be explained by the disruption of polymer chain regularity due to the plasticizing effect of the IL. In case of T_g values, it was observed that the T_g of the sPEEK-2 membrane was similar to the other studies presented in the literature, whereas in this study, the high proton conductive composite membrane obtained by IL doping process (sPEEK$_{1.0}$ -2) showed high T_g value comparing to the IL-doped membrane electrolytes presented in the literature (~ 70–90 °C) [64].

4 Conclusion

In this study, sulfonated poly(ether ether ketone) (sPEEK) and Bronsted acidic ionic liquid (1-methylimidazolium tetrafluoroborate)-based polymer composite membranes were successfully synthesized and characterized for high temperature electrochemical applications. sPEEK polymer matrices were prepared to have three different degrees of sulfonation (32.10, 60.20 and 81.44%). Composite membranes were produced by the addition of ionic liquids (ILs) to the sulfonic acid groups of polymer matrices as equimolar and double (n = 1.0 and 0.5). Sulfonation reaction was proved by ^{1}H NMR analysis. The structures of sPEEK polymer matrices, IL and composite membranes were confirmed by FTIR analysis. sPEEK$_{1.0}$–2 composite membrane showed the highest proton conductivity values (2.50–3.51 × 10^{-1} Sm^{-1}) of all membrane series at a wide temperature range of 380–450 K. As a result of thermogravimetric analysis (TGA), it was observed that all composite membranes maintained their thermal stability above 180 °C. Dielectric measurements were evaluated for the membrane series containing sPEEK$_{1.0}$–2 polymer electrolyte, which shows the highest conductivity. sPEEK$_{1.0}$–2 membrane showed higher dielectric constant (ε') values compared to other electrolytes. When the amount of IL was equimolar to the sulfonic acid groups in the polymer structure, the plasticizing effect of the IL facilitated the orientation of the electric dipoles and consequently increased the ε' values. Similar to ε' values, sPEEK$_{1.0}$–2 sample showed the highest imaginary part of permittivity (ε'') values, while this value is minimum when excess IL was used. Excess IL formed a structure that remains unbound to sulfonic acid groups, and a double layer capacitance can develop due to the ion transfer accumulated between the electrolyte and electrodes. Moreover, with increasing frequency, the available drift time decreased and both the real and imaginary parts of the dielectric constant (ε', ε'') decreased. Low electric modulus (M') values in low frequency regions facilitated ionic mobility. The electrical modulus behavior of sPEEK$_{1.0}$–2 membrane was also compatible with high proton conductivity values. Dynamic mechanic analysis (DMA) results showed that the glass transition temperature (T_g) of sPEEK$_{1.0}$-2 composite membrane was found to be higher than the sPEEK/IL-based polymer electrolytes given in the literature and the composite membrane showed a high maximum stress in anhydrous environment (0.22 GPa). When all these results are evaluated, sPEEK$_{1.0}$-2 composite membrane can be presented as an alternative proton conductive polymeric membrane in electrochemical systems such as HT-PEMFC.

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Author contributions

MY contributed to visualization, writing—original draft preparation, conceptualization, writing, reviewing and editing, investigation, formal analysis.

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Data availability

All data generated or analyzed during this research are included in this published article [and its supplementary information files].

Declarations

Conflict of interest The authors certify that there are no known competing interests associated with this publication and they have no affiliation with or financial involvement in any organization.

Ethical approval Ethics approval was not required for this study.

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