Studies on the SPEEK membrane with low degree of sulfonation as a stable proton exchange membrane for fuel cell applications

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Abstract

Sulfonated poly (ether ether ketone) (SPEEK) with a low degree of sulfonation (DS = 40%) was prepared for proton exchange membrane fuel cells (PEMFC). Poly (ether ether ketone) (PEEK) was sulfonated in concentrated H_2SO_4 under N_2 atmosphere and characterized by the hydrogen nuclear magnetic resonance (H-NMR) technique. After preparation of the SPEEK polymer, the obtained polymer was dissolved in dimethylacetamide (DMAC) solvent and then the solution casting method was applied for the fabrication of membranes. Water uptake behavior, ion exchange capacity (IEC), and the proton conductivity at different temperatures and different relative humidity were determined and compared with a commercial Nafion 117 membrane. The IEC and the proton conductivity results showed that the sulfonation process successfully created   proton conduction channels. In addition, the thermal, mechanical, chemical, and hydrolytic stabilities were thoroughly investigated for the prepared membrane. The low degree of sulfonation SPEEK showed a desirable chemical durability with a higher dimensional, mechanical, and thermal stability than Nafion 117 but lower water uptake and proton conductivity.

1. Introduction

Recently sulfonated poly (ether ether ketone) (SPEEK), a sulfonate-functionalized hydrocarbon polymer, has inspired researchers owing to its noticeable characteristics including thermal and mechanical strength, low price, simple preparation procedure and good film-forming capacity. The most recent research on SPEEK covers various capabilities including biomedical materials [1-3], humidity sensors [4, 5], composite actuators [6], heterogeneous catalysts [7], shape memory polymers [8], dehydration of industrial gases and gas separation membranes [9, 10], water splitting electrodialysis

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devices [11], vanadium redox flow batteries [12], and fuel cells (microbial, direct methanol, alkaline exchange, and proton exchange membranes) [13-18]. Fuel cells, as clean and eco-friendly energy conversion systems, have been widely investigated and gained financial investment for a large number of different applications during the last decades [19, 20]. Proton exchange membrane fuel cells (PEMFCs) are a promising type of fuel cells because of their special characteristics like low-operating temperature, high power density and efficiency, low weight and compactness, fast start-ups, static nature, noiseless feature, tolerance to shocks and vibrations, and safe handling [19, 21, 22]. The proton exchange membrane (PEM) as a key compartments of a PEMFC plays differents roles including proton transfer and separating reactant gases from each other. Commercial Nafion (Dupont), a perfluorinated sulfonic acid (PFSA) membrane, is the current state-of-the-art PEMFC state-of-the-art PEMFCs due to its high proton conductivity at moderate temperatures (<90 °C) and high chemical and mechanical stability. However, this membrane suffers from several practical limitations such as high cost, enviromentaly-unfriendliness relating to the fluorinated structure, low water retention at higher temperature owing to high degree of phase separation and consequently gas cross over, and a major performance reduction at higher temperatures. Some researchers have attempted to use different hydrocarbon ploymers to alter the current proton exchange membranes to a more suitable condition. [13, 21, 23-25].

So far, among different hydrocarbon polymers, SPEEK has shown appropriate properties for fuel cell applications as compared to the Nafion membrane and some of them are commercially available such as the Fumapem membrane (Fumatech) [26]. The chemical structure of SPEEK membranes provide distinct microstructures with different electrochemical and mechanical properties, resulting in certain advantages of SPEEK membranes over Nafion as PEMs [24, 27]. Portale et al. [27] showed a less phase separated structure of SPEEK at high water contents which is the result of a more rigid matrix structure with respect to Nafion. SPEEK and Nafion both have ionic clusters coexisting with the hydrophobic region. However, the nano-separation of hydrophobic and hydrophilic regions is lower for SPEEK compared to Nafion due to the lower acidity of the sulfonic acid groups of SPEEK compared with the fluorinated groups of Nafion, which result in low gas permeation through SPEEK. Additionally, the higher mechanical stiffness of the SPEEK backbone is attributed to the aromatic groups [28, 29].

SPEEK can be straightforwardly synthesized via post sulfonation of PEEK using concentrated sulfuric acid. Different properties of SPEEK have a high dependency on the degree of sulfonation (DS), which can be controlled by adjusting proper reaction conditions (reaction temperature, acid concentration, and sulfonation time). A high DS value offers high proton conductivity closer to that of Nafion; however, this leads to undesirable mechanical properties, excessive dimensional swelling, fuel permeability, and subsequently low durability [23, 30]. Although there are lots of studies about SPEEK and its modifications, most researchers have focused on medium degrees of sulfonation or higher values of degree of sulfonation, and the few publications devoted to SPEEK with low DS possibly arose from its low proton conductivity in a similar condition. As a result, several characteristics of low degree SPEEK membrane are still unknown and need more investigations. To understand the effect of sulfonation on various parameters of a pure SPEEK membrane for different applications and to obtain an advantage in preparation of SPEEK membranes with lower IECs, utilizing a low DS membrane as a model of SPEEK could be pursued as higher degrees could not easily be used owing to their swelling behavior.

In this work, a SPEEK membrane with a low degree of sulfonation was studied and different stability features (thermal, chemical, mechanical, and hydrolytic) and other physicochemical properties were investigated to evaluate its potential applications for PEMFCs.

2. Experimental

2.1. Materials

Poly (ether ether ketone) (PEEK, $\overline{M}w$=20,800, $\overline{M}n$=10,300) was purchased from Sigma-Aldrich Co. Concentrated sulfuric acid (H_2SO_4, 95-97%), N,N-dimethylacetamide (DMAc), sodium chloride (NaCl), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2, 30 wt.%), iron sulfate heptahydrate ($FeSO_4.7H_2O$) were obtained from Merck Co. All materials were analytical grade and have been used as received without further purification. A Nafion 117 membrane was purchased from ElectroChem, Inc. Deionized water (0.7-1.0 MΩ/cm) was used during the experiment (Aquatron, A4000D).

2.2. Preparation of SPEEK membrane

Sulfonation of PEEK was carried out via the post sulfonation method in a three-neck flask with a stirrer bar in concentrated sulfuric acid. Firstly, 100 mL of 95-97% H_2SO_4 was preheated to 50°C under N_2 atmosphere. Then, 5 g of PEEK (previously vacuum dried at 100°C overnight) was added gradually and the sulfonation reaction occurred for 4 h. After sulfonating, the solution was subsequently cooled below 10°C by a water-ice bath to terminate the sulfonation reaction. The obtained polymer solution was decanted into a large amount of ice-deionized water to form SPEEK fibers. Finally, the precipitated SPEEK was washed repeatedly with de-ionized (DI) water until it reached neutral pH. The resulting polymer was dried at 60°C for 12 h followed by further drying at 110°C under vacuum overnight. SPEEK powder was added into DMAc (1 g SPEEK into 10 mL DMAc) with a magnetic stirrer at 45°C for 24 h to have a homogenous polymer solution. The solution was filtered to avoid the presence of fiber-like undissolved polymer in the membrane and then the transparent solution was cast onto a clean flat glass at 60°C for 16 h. Then the membrane was peeled off by immersion in deionized water followed by further drying at 120°C under vacuum for 12 h.

The thickness of the SPEEK membranes was measured (100-120 μm) using a digital micrometer provided by Mitutoyo. Membranes were pretreated before the measurement of proton conductivity and IEC. To this aim, membranes were first immersed in a solution of 0.5 M H_2SO_4 for 1 h and subsequently in DI water at room temperature.

2.3. Characterizations

2.3.1 Membrane characterization

The degree of sulfonation (DS) was determined for the sulfonated polymer using a H-NMR analysis spectra recorded on a Bruker Spectrospin 400 (Ultrashield TM) spectrometer at room temperature. Sulfonated polymer was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) to obtain a 2-5 wt. % solution in the presence of a small amount of tetramethylsilane (TMS) as an internal standard. The cross-section morphology of the membrane sample was studied using a field emission scanning electron microscopy (FESEM, VEGA TESCAN) operated under high vacuum at an accelerating voltage of 20 kV. In addition, energy dispersive x-ray (EDS) was used for elemental analysis of the prepared membrane.

A thermo gravimetric analysis (TGA) test was carried out on a Perkin Elmer (Diamond Pyris model, USA) TGA instrument for about 10 mg membrane under N_2 atmosphere with a heating rate of 10°C min^{-1} from room temperature to 600°C.

Mechanical tensile strength tests were performed according to the standard method (ASTM D 638) using a universal tensile-compression machine under room temperature and humidity with a tensile speed of 10 mm min^{-1}. The size of the membrane samples was 1cm×7cm.

2.3.2. Water uptake (WU) and swelling ratio (SR)

Water uptake and swelling ratio across the thickness was calculated by taking the difference between the corresponding values (weight and thickness) for a wet and dry membrane (Eq. 1 and Eq. 2) [31]. The weight and thickness of the dry membrane was

measured after vacuum drying at 100°C for 24 h. The thickness of the membranes was measured by a digital micrometer provided by Mitutoyo. The thicknesses of five points of each small square membrane were measured and the average was recorded. After that the membrane was immersed in DI water at 25°C for 24 h. The character was measured immediately after removing the surface water by wiping with tissue paper.

$$Water\,uptake\,(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

$$Swelling\,Ratio\,(\%)\ = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \qquad (2)$$

2.3.3. Ion exchange capacity (IEC)

The IEC of the membrane was determined by a classical acid-base titration method. The membrane (in H^+ form) was immersed in 2 M NaCl solution for 48 h. The amount of H^+ released from the membrane was determined by titrating with 0.1 M NaOH solution using phenolphthalein as an indicator. The titrated IEC was obtained from the following formula (Eq.3) [32]:

$$IEC = \frac{V_{NaOH} \times N_{NaOH}}{W_{dry}} (meq.g^{-1}) \qquad (3)$$

Where V_{NaOH} represents the consumed volume of NaOH solution (mL), N_{NaOH} is the molar concentration of NaOH solution (0.1 M), and W_{dry} is related to the weight of the dry membrane.

2.3.4. Proton conductivity

The membrane conductivity was determined as a function of temperature and relative humidity by impedance spectroscopy with a potentiostat/galvanostat (Biologic, SP-150). The membrane was then placed between two polished copper block electrodes quickly hosted in a conductivity cell. The proton conductivity (σ) was calculated using the following formula (Eq.4) [33]:

$$\sigma = \frac{L}{RS} \qquad (4)$$

Where L is the thickness of the membrane, S is the electrode area (determined before conductivity measurements), and R is the resistance of membrane.

2.3.5. Oxidative stability

Small pieces of membrane were soaked in Fenton's reagents (3 wt. % H_2O_2 and 4 ppm Fe^{2+}) [34]. Chemical stability of the SPEEK membrane was measured by recording the degradation time when the membrane degraded completely.

2.3.6 Hydrolytic stability

Hydrolytic stability of the SPEEK membrane was measured through the following procedure: firstly, the membrane was dried at 110°C under vacuum and weighed. Then the membrane was soaked in DI water at 60°C for a determined time and weighed after drying at 110°C under vacuum. The procedure was carried out to 120 h with several determined intervals and the membrane weight changes were checked for each interval.

3. Results and discussion

3.1. H-NMR analysis

Fig. 1 shows the chemical structure of the SPEEK polymer. Different physical and chemical properties of SPEEK are related to the degree of sulfonation theoretically determined by H-NMR. Fig. 2 illustrates the H-NMR spectrum of the prepared SPEEK. The introduction of each sulfonic functional group results in a different signal for the proton at 7.5 ppm. The intensity of this hydrogen signal (represented as H_E) is equivalent to the SO_3H group content and can be used for determination of DS [35]. The DS can be calculated from the following equation (Eq.5) [35]:

$$\frac{n}{12 - 2n} = \frac{A_E}{\sum_{i=A,A',B,B',C,C',D} A_i} , \qquad DS = 100 \times n \qquad (5)$$

where n is the number of H_E per repeat unit, A_E is the peak area of the different H_E signal, and A_i

(i=A,A',B,B',C,C',D) is the peak area of the signals corresponding to all the other aromatic hydrogen (Table 1). Degree of sulfonation was calculated to be 40.23% as reported in Table 2.

3.2. Field emission scanning electron microscopy (FESEM)

Fig. 3a represents the FESEM micrograph of the cross-sectional view of a cryogenically fractured surface of the SPEEK membrane. The image shows a homogeneous and dense morphology, as well as good membrane formation. In addition, a SPEEK polymer with a lower than 30% degree of sulfonation was prepared, but the solubility of that polymer was not very good in the solvent and therefore it did not have good membrane formation. The results showed

Fig. 1. Different types of hydrogen in the SPEEK chemical structure.
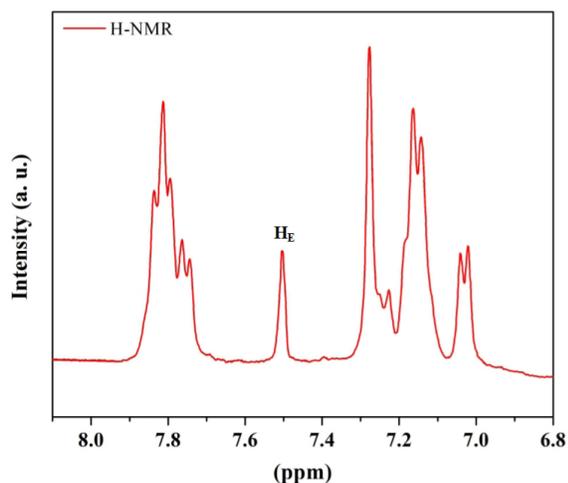
Fig. 2. H-NMR spectra of 4h-SPEEK polymer.

Table 1. Calculating the degree of sulfonation from H-NMR

	H-NMR spectra	Sum of Peak Areas
A, A'	7.68-7.92 ppm	10.0628
B'	6.95-7.06 ppm	2.2512
B	7.15-7.20 ppm	
D	7.07-7.15 ppm	15.5062
C	7.24-7.32 ppm	
C'	7.20-7.24 ppm	
E	7.48-7.52 ppm	1.0000

(a)

(b)
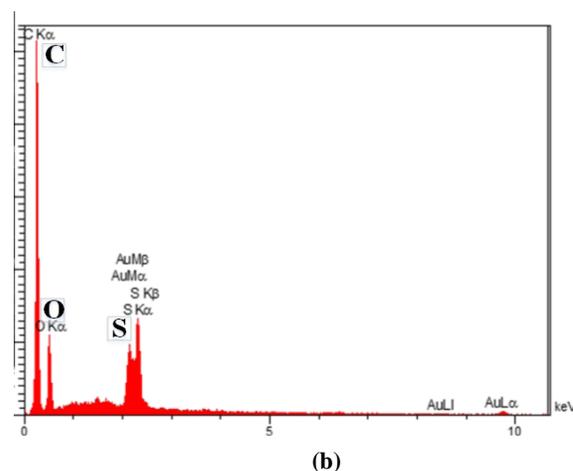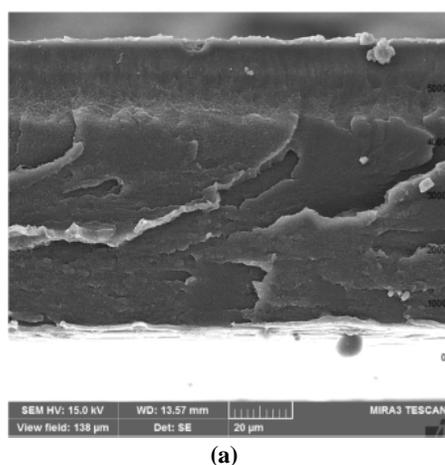
Fig. 3. (a) FESEM image and (b) EDS spectrum of a cross section of the SPEEK membrane.

Table 2. The mechanical properties of 4h-SPEEK and Nafion117 membranes.

Membrane	Young's Modulus, MPa	Tensile Strength, MPa	Fracture Stress, MPa	Elongation at Break, %
4h-SPEEK	2045	73	65	33
Nafion117	126.4	15.7	15.7	130.7

a 40% degree of sulfonation is the appropriate DS for a SPEEK membrane with a low degree of sulfonation because it showed homogeneous and dense morphology. The EDS spectrum of SPEEK (Fig. 3b) showed the presence of C, O, and S elements and supported the sulfonation of polymer.

3.3. Thermo gravimetric analysis (TGA)

Fig. 4 shows the TGA curves and their derivative (DTG) for pure PEEK and SPEEK membranes to identify thermal degradation behavior and the pattern of weight changes throughout the test. PEEK is a type of highly thermo-stable polymer. As shown in Fig. 4a, the starting temperature of its thermal degradation was around 500ºC. After the sulfonation reaction, the produced SPEEK exhibited a different TGA curve. Three weight loss regions were observed in the TGA curves of SPEEK membranes. The first step is related to the evaporation of physically absorbed water and remaining solvent even after vacuum drying during the casting procedure [36, 37], and the next two steps are related to thermal degradation which is also reflected in the DTG curve by two broad peaks [36]. Acid-catalytic splitting-off of -SO_3H groups in membrane structures occurred in the second stage at the temperature range of about 250-440ºC. The third weight loss is connected to the thermal decomposition of polymeric backbone that was observed at about 540ºC starting from 450ºC. 4h-SPEEK membrane were thermally stable up to 250°C and showed appropriate thermal stability [38]
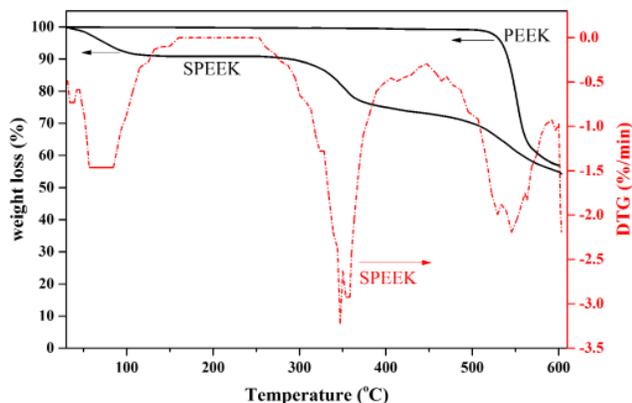
Fig. 4. TGA and DTG curves of SPEEK with 4 h sulfonation reaction and PEEK samples.

for PEMFC application.

3.4. Tensile test

Fig. 5 shows the mechanical stress-strain curves of SPEEK and Nafion 117 membranes at room temperature and humidity. The SPEEK membrane displays a ductile behavior characterized by a yield point followed by neck formation (Fig. 5, inset figure) explained by the fact that the sulfonated polymer was partially amorphous, while the pristine polymer specimen was semicrystalline. The introduction of –SO_3H groups increases chain bulkiness and hinder the entanglement formation. Reduction of entanglements represents lesser topological constraints relative to chain motion below the T_g [38].

The different tensile behavior of SPEEK and Nafion arises from the different microstructure of these two types of polymer. In SPEEK, sulfonic acid groups attached directly to the backbone without any branching which results in higher strength compared with the branched structure of Nafion [39]. It should be noted that these differences affect the water uptake behavior and proton conductivities. Additionally, the yield point of SPEEK is below 10% which is typical for such aromatic hydrocarbon membranes below the T_g [36]. Table 2 shows the mechanical properties of 4h-SPEEK and Nafion117 membranes.
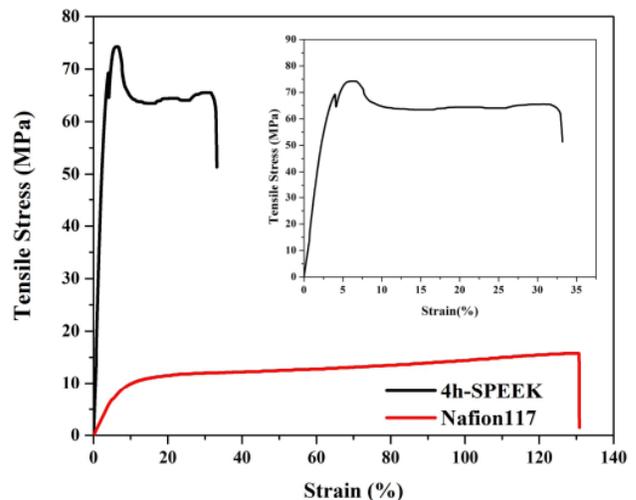
Fig. 5. Mechanical stress-strain curves of SPEEK and Nafion117 membranes. Inset represents the stress-strain curve of the SPEEK membrane.

3.5. IEC, WU and SR

Ion exchange capacity (IEC) as an indicator of the proton conduction sites was measured by the titration method (Table 3). The results show higher ion exchange capacity of SPEEK compared to commercial Nafion. In addition, the experimental value of DS was calculated using the following formula (Eq.6) [40]:

$$DS = 100 \times \left(\frac{288.30 \times IEC}{1000 - 102.05 \times IEC} \right) \qquad (6)$$

The results show good agreement between the theoretical and experimental values (DS_{H-NMR} and DS_{IEC}, respectively).

The water uptake of hydrated ionic-conducting polymers is an essential requirement for many of their important properties including mechanical behavior and conductivity [43]. With the aim of providing a reasonable proton conductive membrane, in addition to sufficient proton exchange sites, water uptake plays an important role supplying a suitable medium for the two principal mechanisms of proton transfer (hopping or Grotthuss and vehicle) [44]. Table 3 represents the water uptake and the hydration number (λ, nH_2O/nSO_3^-) of SPEEK and commercial Nafion. Results show lower water uptake and swelling ratio for 4h-SPEEK compared to Nafion 117.

3.6. Proton conductivity

Proton conductivity, as the most necessary requirement for proton exchange membranes, was measured vs. temperature changes at two different relative humidity (100% and 60% RH) (Fig. 6a.). It was obvious from the figure that proton conductivity is enhanced by increasing the temperature and relative humidity. When the temperature rises, intermolecular forces decrease and mobility increases resulting in higher swelling, increased ionic cluster density, higher water uptake, and subsequently more proton conductivity [27, 45]. Fig. 6a illustrates lower values for 4h-SPEEK rather than its higher ion exchange capacity compared to Nafion117. The observations could be due to dead-end paths and some non-contributing sulfonic acid sites in proton conduction of SPEEK which are a result of the low phase separation of such membranes. The high proton conductivity of Nafion is due to its well-developed hydrophilic/hydrophobic phase separation [39]. The different structural characteristic of these two types of membrane (PFSA type and hydrocarbon type) that have an influence on proton conductivity are comprised of the width of proton conduction paths, connectivity between proton conductive regions, dead-end sulfonic acid groups, phase segregation, proximity of proton exchange sites, and the tortuosity and porosities of nano-channels inside the membrane [39, 46-48].

The activation energies of proton conduction at these two RH (60% and 100%) were calculated by linear regression on Arrhenius plots using the following relation (Eq. 7) [33]:

$$\sigma = A e^{-\left(\frac{E_a}{RT} \right)} \qquad (7)$$

Table 3. DS of the SPEEK sample and IEC, WU, and SR for SPEEK and Nafion117 [41, 42].

	4h-SPEEK	Nafion
DS_{H-NMR} (%)	40.23	-
IEC (meq/g)	1.23	0.91
DS_{IEC} (%)	40.24	-
WU (%)	6.29	12.41
λ †	2.84	7.58
SR (%)	< 3%	< 10%

† $\lambda \left(\frac{nH_2O\,(mol)}{SO_3^-\,(mol)} \right)$ the hydration number or water uptake coefficient, was calculated using $\lambda = \frac{10 \times WU}{IEC \times MW_{H_2O}}$ where MW_{H2O} is 18.02 mol.gr^{-1} [41, 42]

where σ (mS cm^{-1}) is the proton conductivity, A is the frequency factor, E_a (kJ mol^{-1}) is the minimum activation energy of proton conduction, R (8.314 J mol^{-1}K^{-1}) is the universal gas constant, and T (K) is the absolute temperature.

The results (Fig. 6b) demonstrated that E_a decreases as RH increases which show that proton conductivity is related to the water uptake, which is in turn related to mechanical properties of the membrane [42]. The hydration–conduction relationship is also related to the aforementioned structural factors. Water content increments result in widening of the nano-channels due to the plasticization effect of water [38, 43], enhancement of the proton carriers, and subsequently decrement of the energy barrier of proton conduction (E_a).

3.6. Oxidative and hydrolytic stabilities

Chemical stability of PEM against the reactive oxygen species has a major significance in long term durability of the membrane. Actually, the free radicals attack the sensitive sites of the polymer chain and create more destructive radicals, which again attack the polymer chain repeatedly [49-51]. PEEK is a highly stable chemical polymer but when sulfonic acid groups attach this polymer, the stability of the membrane decays. In this research, by focusing on this parameter a SPEEK membrane with a low degree of sulfonation was prepared and Fenton's ex situ test was applied as an accelerated degradation analysis to evaluate the endurance behavior of the membrane through this aging parameter. The results (Table 4) show 200 minute durability in Fenton's solution at 68 °C for this low degree SPEEK membrane which is considered suitable for PEMFC applications.

The durability of PEMs is usually determined by Fenton's test, but the loss of mechanical strength after a long humidification time could influence the strength, unfortunately there isn't any clear distinction
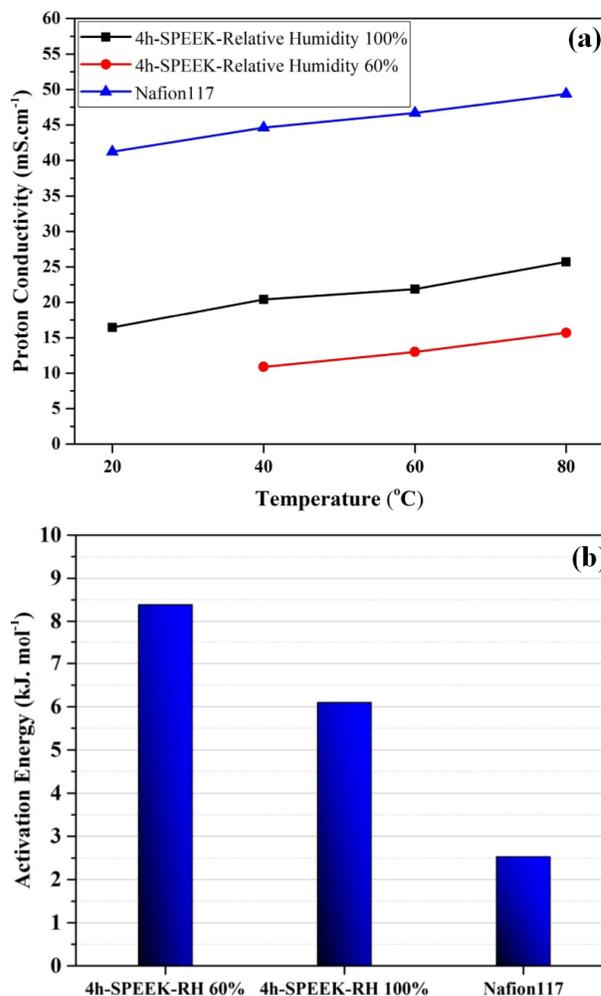
Fig. 6. Proton conductivities and activation energies of SPEEK (RH=60 and 100%) and Nafion117 (RH=100%) membranes as a function of temperature and relative humidity.

between chemical and mechanical degradations. Sufficient water content supplies proton conductivity, but it could also affect the hydrolytic stability and simultaneously chemical stability as limiting factors on the long term life of the membrane [50, 52-55]. In fact, highly polar water molecules undermine the electrostatic interactions (Van der Waals interactions) between SPEEK molecular chains due to their high dielectric constant, as a plasticizer that

Table 4. Hydrolytic and Oxidative Stability of 4h-SPEEK

Hydrolytic stability (remaining weight, wt. %)	77
Oxidative stability (min)	200

causes swelling, lowers the elasticity of membrane and affects the durability [38, 43]. The hydrolytic stability results of the prepared SPEEK membrane during 120 h was studied (Fig. 7). The results show about 77 % remaining weight of membrane after the test (Table 4). The main weight loss was observed in the first 60 h, after that the weight did not show any considerable changes.
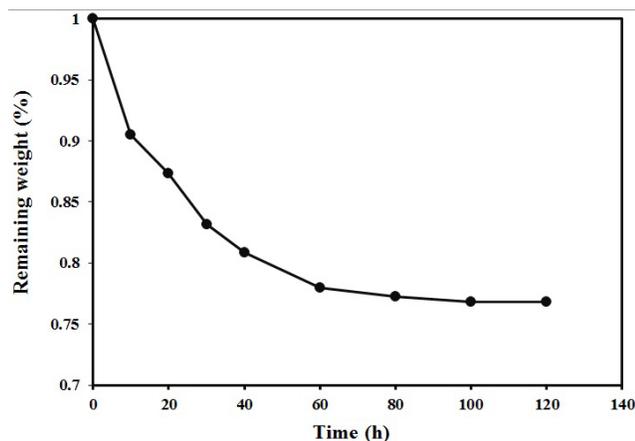
Fig. 7. Hydrolytic stability of the SPEEK membrane at 60°C during 120 h.

4. Conclusions

In this work, a sulfonated poly (ether ether ketone) (SPEEK) membrane with a low degree of sulfonation was prepared. FESEM results showed homogeneous and dense morphology and good membrane formation. Thermal, mechanical, chemical, oxidative and hydrolytic stabilities, uptake behavior, IEC, and proton conductivity at different temperatures and relative humidity were determined. The characterization results showed that the thermal stability of the polymer decreased after sulfonation. The membrane had higher thermal and mechanical stability than commercial Nafion 117 with reasonable oxidative stability, but lower water uptake and proton conductivity required more study and modification. A SPEEK membrane with a low degree of sulfonation would be a proper alternative stable membrane for PEMFC applications if the low proton conductivity barrier could be overcome with more controlled and adjusted procedures.

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