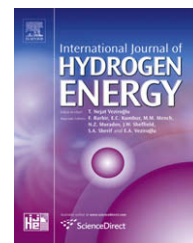


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# Preparation and characterization of sulfonated polysulfone/titanium dioxide composite membranes for proton exchange membrane fuel cells

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## ABSTRACT

In the present study, sulfonated polysulfone (sPS)/titanium dioxide (TiO<sub>2</sub>) composite membranes for use in proton exchange membrane fuel cells (PEMFCs) were investigated. Polysulfone (PS) was sulfonated with trimethylsilyl chlorosulfonate in 1,2 dichloroethane at ambient temperatures. It was shown that the degree of sulfonation is increased with the molar ratio of the sulfonating agent to PS repeat unit. The degree of sulfonation was determined by elemental analysis and <sup>1</sup>H NMR was performed to verify the sulfonation reaction on the PS. Sulfonation levels from 15 to 40% were easily achieved by varying the content of the sulfonating agent. Composite membranes were prepared by blending TiO<sub>2</sub> with sPS solution in DMAC (5 wt.%) by the solution casting procedure. The membranes have been characterized by thermal analysis, water uptake, proton conductivity measurements and single cell performance. The addition of TiO<sub>2</sub> increased the thermal stability but high filler concentrations decreased the miscibility of the composite component, and resulted in brittle membranes. The conductivity values in the range of 10<sup>−3</sup>–10<sup>−2</sup> S/cm were obtained for composite membranes. The conductivities of the membranes show similar increasing trend as a function of operating temperature. The membranes were tested in a single cell operating at 60–85 °C in humidified H<sub>2</sub>/O<sub>2</sub>. Single fuel cell tests performed at different operating temperatures indicated that sPS/TiO<sub>2</sub> composite membrane is more hydrodynamically stable and also performed better than sPS membranes. The highest performance of 300 mA/cm<sup>2</sup> was obtained for sPS/TiO<sub>2</sub> membrane at 0.6 V for an H<sub>2</sub>–O<sub>2</sub>/PEMFC working at 1 atm and 85 °C. The results show that sPS/TiO<sub>2</sub> is a promising membrane material for possible use in proton exchange membrane fuel cells.

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## 1. Introduction

Fuel cells represent a promising energy source for portable devices, automobiles, and stationary appliances. Among

various types of fuel cells, the proton exchange membrane fuel cell (PEMFC) is attracting much interest, because it is capable of producing high power densities working at low temperatures [1].

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Proton exchange membrane, as the proton conductive material is a key component of the PEMFC for transferring protons from the anode to cathode as well as providing a barrier to the fuel gas cross-leaks between the electrodes [2].

Perfluorosulfonic acid type membranes, the best known example of which is DuPont's Nafion, are most widely used both in fuel cell research and industry. Nafion is commonly used as a polymer electrolyte membrane because of its high proton conductivity, excellent mechanical properties, and good chemical stability. However, the high cost, low stability at high temperatures, low conductivity at low humidity or high temperature and high methanol crossover of Nafion limit the extent of its further application and commercialization [3,4].

Recently, alternative materials to Nafion have been developed with non-perfluorinated backbone chains that have high thermal, thermo-oxidative, chemical, and mechanical stabilities with lower costs. Polysulfones (PS) are commercially available materials, well known for their excellent mechanical, thermal, and chemical stability. The low cost and ease of processing have permitted many research groups all over the globe to focus on their properties and characteristics. These aromatic polymers have been sulfonated by treatment with various sulfonating agent to produce proton-conducting materials [5,6]. The hydrophobic domains formed by non-sulfonated polymer segments provide the hydrated proton exchange membranes with mechanical strength, whereas the hydrophilic domains containing the sulfonic acid groups ensure the proton conductivity [7].

Several researchers have investigated the use of chlorosulfonic acid as a sulfonating agent for several aromatic polymers. Chlorosulfonic acid was employed in an electrophilic substitution reaction to introduce ionic groups along the aromatic polymers. The room temperature sulfonation reactions were conducted for different time intervals to yield polymers with different levels of sulfonation. However, chlorosulfonic acid causes undesirable and detrimental side reactions, such as chain scission, branching and/or cross-linking at the isopropylidene group of the polysulfone. Recently, several researchers used trimethylsilyl chlorosulfonate to sulfonated polysulfone. The silyl-protected reagent reportedly minimized chain scission, as determined by viscosity experiments [8–10].

The polymeric/inorganic composite membranes have attracted great attention because of their dual functionality like specific chemical reactivity and flexibility of the organic polymer backbone, as well as the mechanical properties and thermal stability of the inorganic backbone [11]. In recent years, organic–inorganic composites have been investigated for hydrogen PEMFC with the main objective of increasing the performance of the membrane. Composite membranes based on zeolites [12],  $\text{TiO}_2$  [13,14] and zirconium hydrogen phosphonates [15,16] have been investigated with improvements reported in many properties relative to their matrix materials. Among the inorganic materials used in this field,  $\text{TiO}_2$  is a good candidate as hydrophilic filler for the polymer membranes because it helps to maintain a suitable hydration of the membrane under fuel cell operating conditions, and the mechanical properties are improved [17].  $\text{TiO}_2$  also has good compatibility with organic solvents used to prepare PS casting

solutions. These properties allow access to a very stable and homogeneous dispersion without agglomeration. The hydrophilicity and mechanical and thermal stability are also enhanced because of the increase in the viscosity of suspension, and the strong interaction between  $\text{TiO}_2$  and the polymers [18].

In the present study, sPS was successfully produced using trimethylsilyl chlorosulfonate by post-sulfonation method. Trimethylsilyl chlorosulfonate was generated by chlorotrimethylsilane and chlorosulfonic acid to minimize side reactions with the polymer. Additionally, sPS/ $\text{TiO}_2$  composite membranes were prepared using *N,N*-dimethylacetamide (DMAC) as casting solvent and  $\text{TiO}_2$  as inorganic filler. A series of properties of resulting membranes including water uptake, thermal properties and proton conductivity was examined to investigate the relationship between the membrane structure and its properties. The performance of the sPS membranes was compared with the composite membrane in a single cell  $\text{H}_2$ – $\text{O}_2$ /PEMFC.

## 2. Experimental

### 2.1. Materials

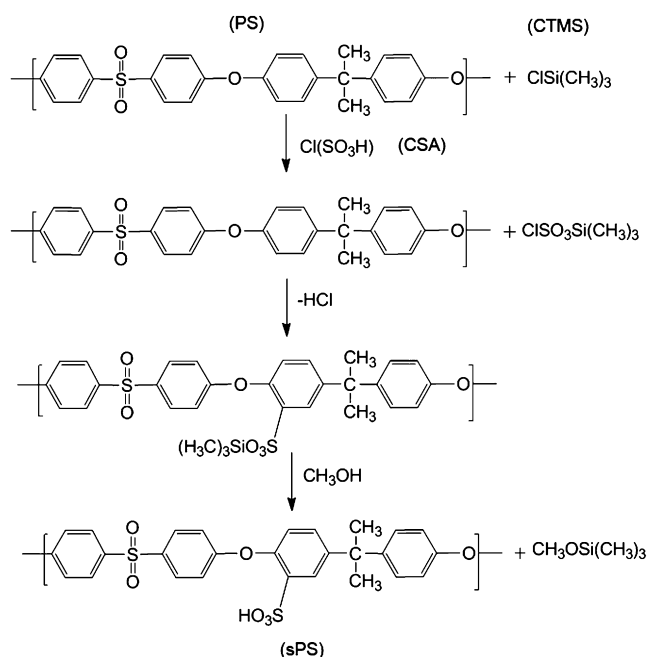
Polysulfone polymer was obtained from Aldrich (USA). Chlorosulfonic acid ( $\text{HSO}_3\text{Cl}$ , 99%) and chlorotrimethylsilane ( $(\text{CH}_3)_3\text{SiCl}$ , 98%) were used as received.  $\text{TiO}_2$  was obtained from Degussa (P25) was used as received. *N,N*-dimethylacetamide ( $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$  DMAC), 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ , DCE) and *N*-methyl-2-pyrrolidone ( $\text{C}_5\text{H}_9\text{NO}$ , NMP) were used as received. All solvents used were high grade reagents.

### 2.2. Sulfonation of polysulfone

The PS was sulfonated according to a procedure described by Chao et al. [19]. The dried PS was dissolved in 100 ml anhydrous 1,2-dichloroethane in a 250 ml three-neck flask equipped with mechanical stirrer, condenser and nitrogen purge inlet which carries the gaseous HCl generated by the substitution. The reaction scheme is given in Scheme 1. The resulting solution was purged with nitrogen for 1 h and chlorotrimethylsilane was added to the solution, followed by dropwise addition of chlorosulfonic acid diluted in 20 mL 1,2 dichloroethane for 30 min. The amount of intermediate product depends on the mole ratio of sulfonating agent and polymer-repeating units. The resulting solution was vigorously stirred for 12 h at 30 °C. After reaction was completed, sPS was isolated from the solution by precipitation with methanol, and then the polymer was washed with deionized water for several times and dried to constant weight at 60 °C under vacuum. The molar ratio of PS:CSA was 1:0.5, 1:0.8 and 1:1. In case of higher chlorosulfonic acid content, the sulfonated polymer produced was water soluble.

### 2.3. Polymer characterization

Degree of sulfonation was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and elemental analysis.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of polymers were recorded on a spectrometer (JEOL 6×-



**Scheme 1 – Sulfonation reactions of polysulfone.**

400, 400 MHz) with DMSO- $d_6$  as a solvent at 27 °C. Elemental analysis of polymers based on sulfur to carbon ratio was performed by using CHNOS Elemental Analyzer (Vario EL II).

Fourier transform infrared spectra of the polymers were recorded with an FTIR spectrometer (Nicolet 510, USA) in the 4000–400  $\text{cm}^{-1}$  range, where 30 scans were taken at 4  $\text{cm}^{-1}$  resolution.

Viscosity measurements were determined by Cannon Ubbelohde viscometer in *N*-methyl-2-pyrrolidone at 25 °C.

Glass transition temperature ( $T_g$ ) of sPS polymers was determined by DSC analyzer (DuPont-TA 910S) at a heating rate of 10 °C/min under nitrogen atmosphere.

#### 2.4. Membrane preparation and characterization

Homogeneous membranes were cast from polymer solutions with a concentration of 10 wt.% in *N,N*-dimethylacetamide (DMAC). After casting, DMAC was evaporated in a vacuum oven at 60 °C for 24 h. For further removal of any residual solvent, the membranes were immersed in a water bath at 60 °C for 48 h, and dried. The sPS membranes were converted to their acid form. The membranes were placed in 1.5 M aqueous sulfuric acid solution at 30 °C for 24 h and then washed with deionized water several times. All membranes were stored in deionized water before any test was performed. Before MEA preparation the membrane was treated by boiling in  $\text{H}_2\text{SO}_4$  solution (0.5 M) about 1 h and washing in DI water for half an hour.

The composite sPS/ $\text{TiO}_2$  membranes were prepared by the following procedure: an appropriate amount of 10% polymer solution was mixed with  $\text{TiO}_2$  in an ultrasonic bath for 1 h. The resulting solution was cast in a Petri dish by heating at 80 °C for 24 h. The membrane was removed from the Petri dish by wetting with deionized water.

Thermal stability of the polymer membranes was examined for the temperature range of 25–850 °C at a heating rate of

10 °C/min under nitrogen atmosphere using a Thermal Analyzer (DuPont-TA 951).

The X-ray powder diffraction (XRD) analysis was performed using an X-ray diffractometer (Rigaku D-MAX 2200, Japan) with Cu  $K\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation over the range  $5^\circ \leq 2\theta \leq 100^\circ$ .

Swelling behavior is regarded as one of the most important characteristic properties for the sPS membranes, which confirm the successful incorporation of hydrophilic group inside the membrane. The membranes were soaked in water at 80 °C for 24 h. The excess water was wiped off gently with a foam filter and they were then weighed immediately. Subsequently, the membrane samples were dried at 100 °C in vacuum to constant weight. The swelling index (SI) was calculated using the following equation [20]:

$$\text{SI} = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100\% \quad (1)$$

where,  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the water-swollen and dry membrane sample, respectively.

#### 2.5. Proton conductivity analysis

The proton conductivity of the membranes was measured by AC Electrochemical Impedance Spectroscopy (EIS) technique over a frequency range of 1–300 kHz with an oscillating voltage using the potentiostat system (GAMRY PCL40). All measurements were performed in longitudinal direction; in air/water vapor atmosphere at 100% relative humidity with 4-probe EIS as a function of temperature. The specimens were prepared as 1 cm × 5 cm membrane strips and sandwiched into Pt electrode lined Teflon conductivity cell. The specimen and the electrodes were fixed by nuts and bolts. The specific conductivity [ $\sigma$  ( $\Omega \text{ cm}$ ) $^{-1}$ ] was calculated on the basis of the measured resistance according to the following equation [21]:

$$\sigma = (1/R) \times (l/A) \quad (2)$$

where  $l$  is the distance between the two electrodes (cm),  $R$  is the membrane resistance ( $\Omega$ ) and  $A$  is the cross-sectional area of the membrane ( $\text{cm}^2$ ).

#### 2.6. Membrane electrode assembly (MEA) preparation

MEAs were prepared by spraying catalyst ink onto the gas diffusion layers (GDLs 31 BC, SGL Carbon, Germany) [22]. In the first step, catalyst ink, which is comprised of 20 wt.% Pt on Vulcan XC-72 catalyst (E-Tek), 5 wt.% Nafion solution (Ion Power Inc.), distilled water, and 2-propanol, were prepared and mixed in ultrasonic bath for 2 h. In order to coat the GDLs with catalyst layer, the anode and cathode side GDLs were fixed on a paper frame. The catalyst ink was sprayed until the desired catalyst loading (0.4 mg Pt/ $\text{cm}^2$  for both anode and cathode sides) was achieved. The catalyst loading was controlled by weighing the GDLs at different times. After the GDLs were loaded with catalyst, they were kept in oven at 80 °C for 1 h in order to completely remove the liquid components of catalyst ink. Then, they were weighed again. After spraying the catalyst ink onto the GDLs, MEA was prepared by pressing these GDLs onto the treated membrane at 130 °C, 688 N/ $\text{cm}^2$  for 3 min.

## 2.7. PEMFC performance tests

Performances of fabricated MEAs were measured via the PEMFC test station built at METU Fuel Cell Technology Laboratory. A single PEMFC (Electrochem FC05-01SP-REF) with a 5 cm<sup>2</sup> active area was used in the experiments. The external load was applied by means of an electronic load (Dynaload® RBL488), which can be controlled either manually or by the computer. The current and voltage of the cell were monitored and logged throughout the operation of the cell by the fuel cell test software (FCPower® v. 2.1.102 Fideris). The fabricated MEA was placed in the test cell and the bolts were tightened with a torque of 1.7 Nm on each bolt. The cell temperature was adjusted and the temperatures of the humidifiers and gas transfer lines were set 10 °C above the cell temperature. After

the preset temperatures were reached, hydrogen and oxygen are supplied to the cell at a rate of 0.1 slpm. The cell was operated at 0.5 V until it came to steady state. After steady state was achieved, starting with the OCV value, the current–voltage data were logged by changing the load.

## 3. Results

### 3.1. The effect of degree of sulfonation on the properties of sulfonated polysulfones

Fig. 1 illustrates the representative <sup>1</sup>H NMR spectrum of PS and sPS. The proton resonance at ~7.72 ppm is assigned to the proton adjacent to the new pendent sulfonic acid. Degree of

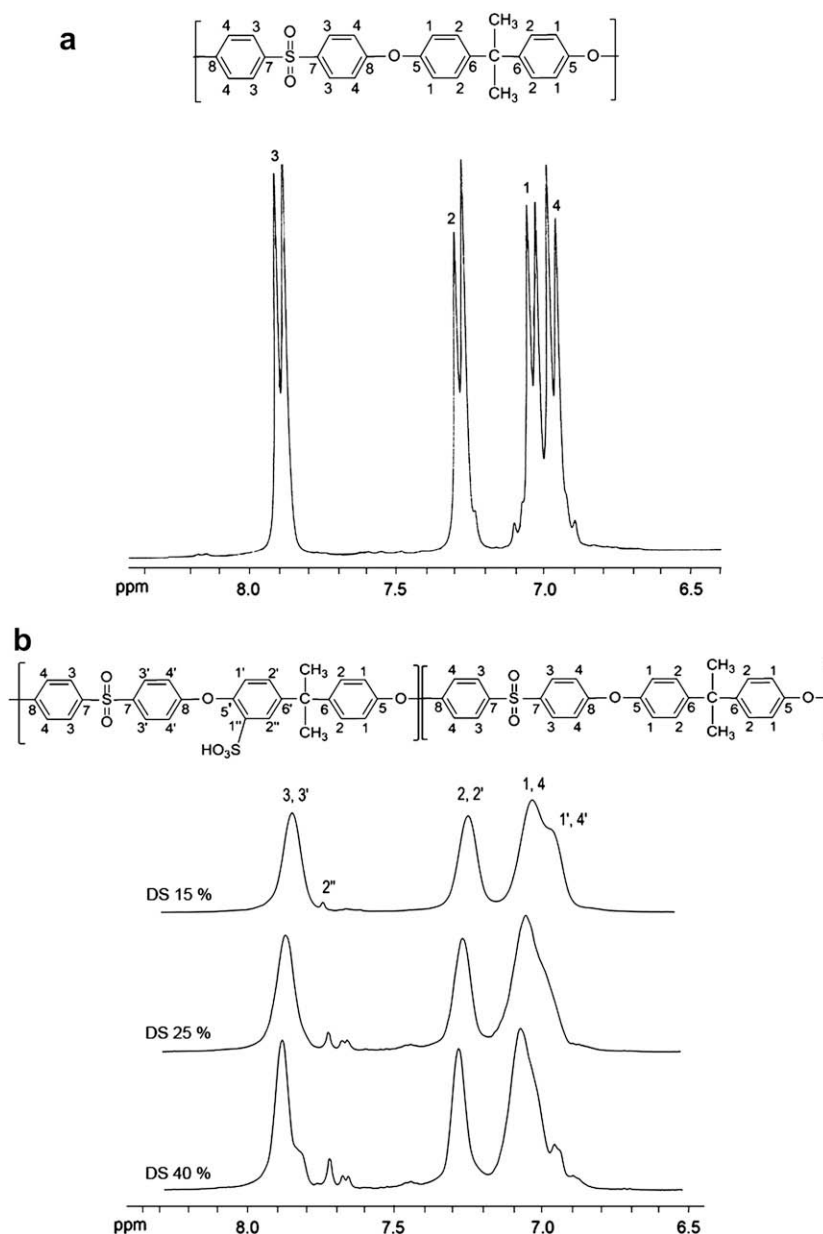


Fig. 1 – <sup>1</sup>H NMR spectra of (a) polysulfone, PS and (b) sulfonated polysulfone, sPS with different sulfonation degrees (DS) 15%, 25% and 40%.

sulfonation of PS was determined similarly as reported in the literature [23]. Using the integration of this proton and a known proton, one is able to determine the actual degree of sulfonation. The degree of sulfonation was also determined by elemental analysis of sPS polymers based on sulfur to carbon ratio. Degree of sulfonation results calculated from  $^1\text{H}$  NMR and elemental analysis were comparable and these results are shown in Table 1.

FTIR analysis has been used to analyze characteristic bands corresponding to the sulfonate groups in different polymers, e.g. sulfonated poly(arylene ether sulfone)s, polystyrene, and poly(phenylene sulfide) [24]. The FTIR spectra of sPS with different degrees of sulfonation are reproduced from 500 to  $1600\text{ cm}^{-1}$  in Fig. 2. Strong characteristic peaks for FTIR spectra at  $1030$  and  $1098\text{ cm}^{-1}$  were observed for all the sulfonated polymers, and they were assigned to symmetric and asymmetric stretching of the sulfonate group. The intensity of these two characteristic peaks increased with increasing degree of sulfonation as the content of the sulfonate groups increased from 10 to 50 mol%. The  $\text{SO}_2$  symmetric stretching was observed at  $1150\text{ cm}^{-1}$  and para in-plane aromatic C–H bond could be detected at  $1107\text{ cm}^{-1}$ . FTIR and  $^1\text{H}$  NMR analysis confirmed the successful electrophilic substitution of trimethylsilyl chlorosulfonate and chloro sulfonic onto PS.

As shown in Table 1, the intrinsic viscosities of sPS increased with increasing degree of sulfonation. The increase in intrinsic viscosity is attributed to the increase in hydrodynamic size of the sulfonated polymer chain relative to the unmodified polymer chain.

### 3.2. Thermal characteristics of polymers and membranes

The influence of degree of sulfonation on the glass transition temperature,  $T_g$  of sPS polymer was reported in Table 1. The DSC data showed an increase in  $T_g$  ( $189$ – $205^\circ\text{C}$ ) in the range  $15$ – $40$  mol% of  $\text{SO}_3$  groups. The introduction of  $\text{SO}_3$  groups increases the intermolecular interactions by pendent ions or hydrogen bonding and molecular bulkiness, which hinder the internal rotation of high molecular chain segments and lead to increased  $T_g$ s of sPS [25].

TGA analysis of PS, sPS and sPS/ $\text{TiO}_2$  membranes was reported in Fig. 3. The parent PS is a highly thermostable polymer, of which the 5% weight loss temperature is above

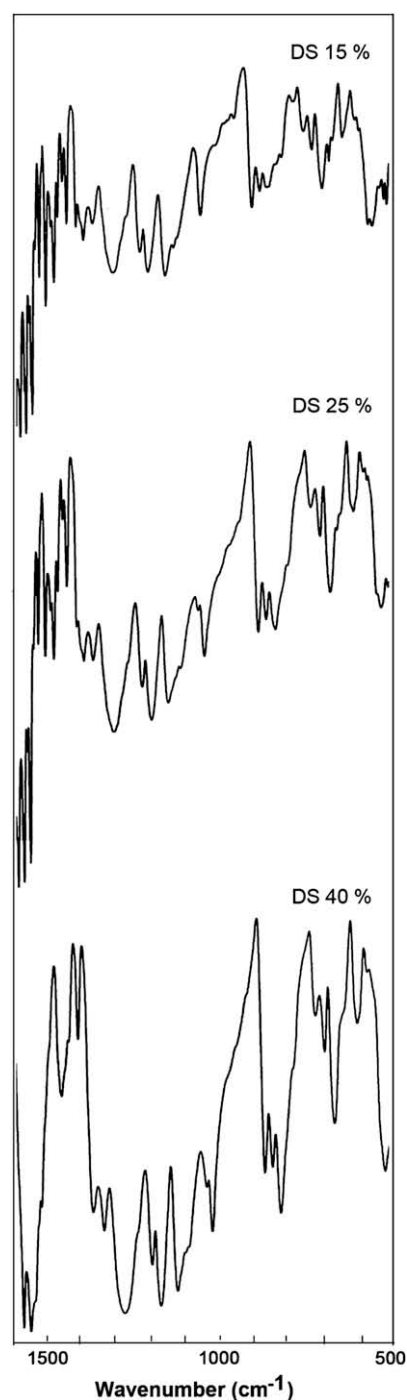


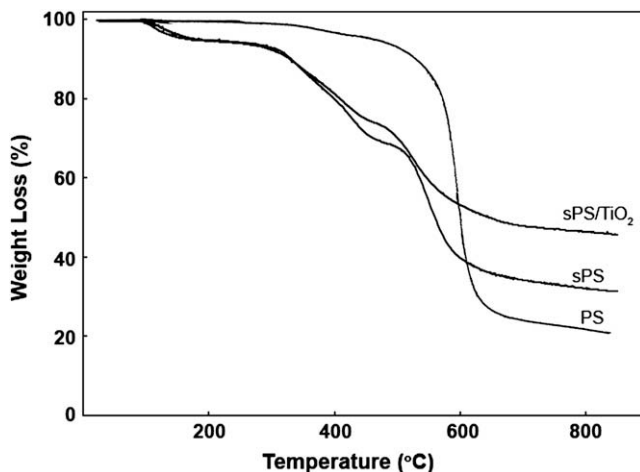
Fig. 2 – FTIR spectra of sulfonated polysulfone sPS, with different sulfonation degrees.

Table 1 – Sulfonation degree, glass transition temperature ( $T_g$ ) and intrinsic viscosities ( $\eta$ ) of sulfonated polysulfone.

Molar ratio of PS:CSA	Sulfonation degree (%)		Glass transition temperature ( $T_g$ ) ( $^\circ\text{C}$ )	Intrinsic viscosity ( $\eta$ ) (dl/g)
	by $^1\text{H}$ NMR	by Elemental analysis		
1:0	–	–	185	0.50
1:0.5	15	14.8	189	0.54
1:0.7	25	25.7	198	0.68
1:1	40	41.0	205	0.79

$500^\circ\text{C}$ , and there is only one weight loss step that is ascribed to the decomposition of polymer main chain. For the sPS, three transitions of weight loss in three separate temperature ranges can be distinguished in the figure. The first step around  $100^\circ\text{C}$  is related to the loss of the absorbed water. The second one, between  $300^\circ\text{C}$  and  $450^\circ\text{C}$ , can be attributed to the decomposition of the  $-\text{SO}_3\text{H}$  groups. The third thermal degradation of sPS at about  $500^\circ\text{C}$  is assigned to the degradation of the polymer main chain. Similar observations were



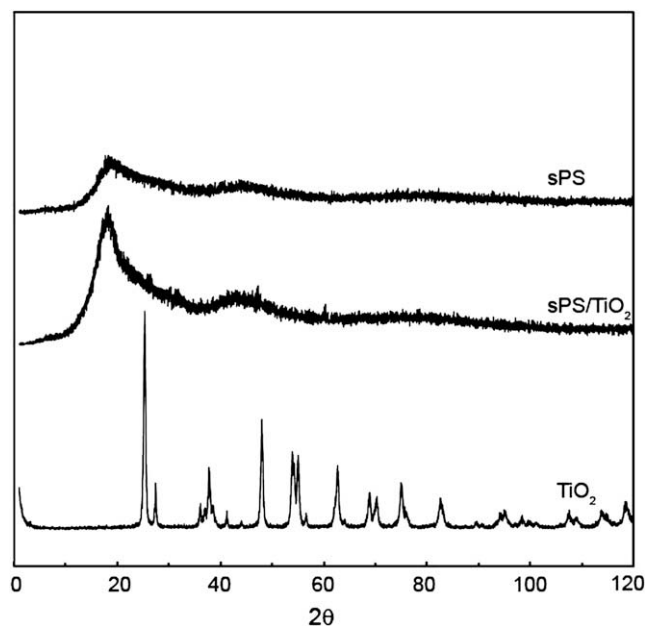


**Fig. 3 – TGA curves of polysulfone PS, sulfonated polysulfone sPS (40% sulfonation) and sPS/TiO<sub>2</sub> composite membranes.**

made for other sulfonated high performance polymers [26,27]. TGA results also suggest that the sPS/TiO<sub>2</sub> composite has slightly higher thermal stability than neat sPS. The residual percentages of sPS and sPS/TiO<sub>2</sub> composites after TGA analysis in nitrogen are 31.5 and 45.7%, respectively.

### 3.3. Results of XRD analysis

The XRD diffraction patterns of sPS membrane, sPS/TiO<sub>2</sub> composite membrane and TiO<sub>2</sub> were illustrated in Fig. 4. The base PS polymer is known to be an amorphous polymer with a rigid polymer structure. The pattern of sPS/TiO<sub>2</sub> composite



**Fig. 4 – XRD patterns of sulfonated polysulfone sPS (40% sulfonation), sPS/TiO<sub>2</sub> composite membranes and TiO<sub>2</sub> composite membranes.**

**Table 2 – Water uptake and proton conductivity of sulfonated polysulfone and sulfonated polysulfone/titanium dioxide composite membranes.**

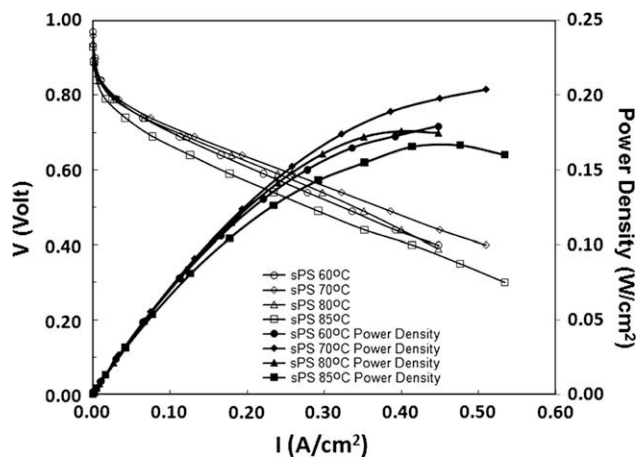
Membrane	Sulfonation degree (%)	Water uptake (%)	Proton conductivity, $\sigma$ (S/cm)		
			30 °C	50 °C	90 °C
sPS-1	15	7	0.004	0.012	0.021
sPS-2	25	17	0.007	0.031	0.046
sPS-3	40	33	0.014	0.065	0.120
sPS/TiO <sub>2</sub>	40	29	0.012	0.061	0.098

membrane has three crystalline characteristic peaks at  $2\theta$  of 26.25°, 38.12°, 49.35° that is analogous with the characteristic peaks of TiO<sub>2</sub> crystal powders in addition to the dispersion peak of sPS [28]. Due to the low concentration of TiO<sub>2</sub> (10%) in sPS/TiO<sub>2</sub> composite membrane only characteristic peaks could be seen in XRD patterns [29]. However their locations are slightly shifted, when compared with the pattern of TiO<sub>2</sub> nanoparticles. This shift of characteristic peaks of TiO<sub>2</sub> in the sPS/TiO<sub>2</sub> composite membrane indicates that there may be interactions between polymer and TiO<sub>2</sub> [30].

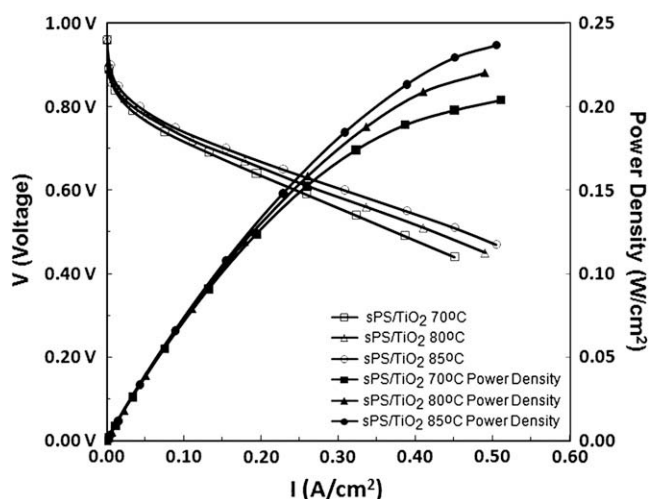
### 3.4. Water uptake and proton conductivity

The water uptake and proton conductivity of the sPS and sPS/TiO<sub>2</sub> composite membranes are listed in Table 2 as a function of sulfonation degree. The water uptake of the sPS membranes was increased from 1 to 33% with increasing degree of sulfonation. This is due to the fact that the sulfonic acid groups are hydrophilic and hence the membranes with higher sulfonation can absorb more water [31]. At the same sulfonic acid content, water uptake of the sPS/TiO<sub>2</sub> composite membranes is lower than sPS membrane; because of the presence of inorganic matter to reduce the membrane free volume and swelling ability [32].

As shown in Table 2, the proton conductivity of sPS membranes increased with sulfonic acid content and



**Fig. 5 – Effect of sulfonation level and operating temperature on the performance of sulfonated polysulfone (sPS) membranes.**



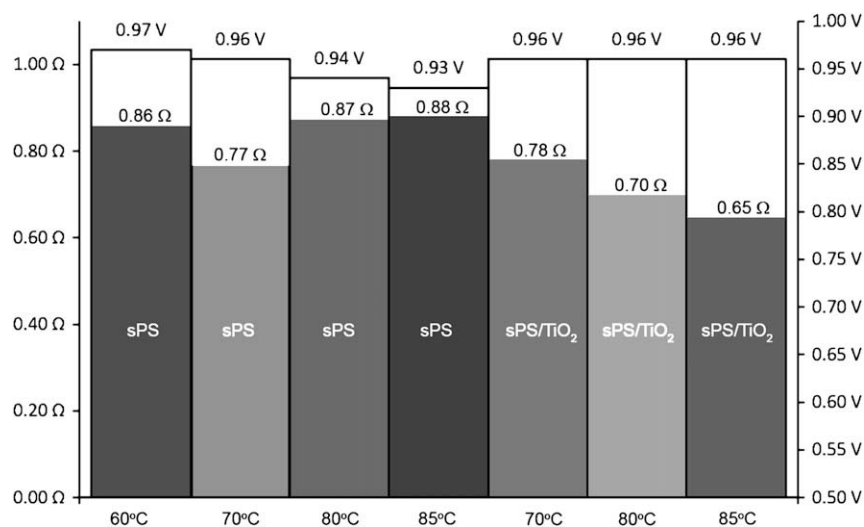
**Fig. 6 – Effect of operating temperature on the performance of sPS/TiO<sub>2</sub> composite membrane.**

maximum conductivity of 0.12 S/cm was reached at 100% relative humidity and at 90 °C. Proton transfer is enhanced by increasing the number of acid sites. Proton conductivity of the sPS/TiO<sub>2</sub> composite membrane increases with temperature, relating to high thermal stability in the structure and sulfonic acid group. sPS/TiO<sub>2</sub> composite membrane proton conductivity was 0.098 S/cm at 90 °C.

### 3.5. Single cell tests

The polarization curves obtained at different cell temperatures for the membrane electrode assemblies (MEAs) prepared with sPS membranes and sPS/TiO<sub>2</sub> composite membranes are shown in Figs. 5 and 6, respectively. The potential losses at the low current densities shown in a polarization curve are said to be activation polarization which is directly related to the reaction kinetics. In addition to kinetic losses, at OCV

conditions or at very low current operating conditions, internal currents or reactant crossover losses may have dramatic effects on cell potential. The difference between the measured and theoretical OCVs is mainly caused by two factors: one voltage drop is linked with the reaction between the platinum surface and oxygen, the other one is due to the hydrogen crossover/internal currents through the electrolyte. In the present work since the same electrodes having platinum catalyst are used for both sPS and sPS/TiO<sub>2</sub> composite membranes at the identical gas compositions and flow rate, pressure and temperature conditions, the difference in the OCV values is attributed to the crossover of the hydrogen to the cathode [33,34]. When the low current density behavior of the MEA prepared with sPS membrane is analyzed, it is seen that the temperature increase does not result in a potential increase, but it remains roughly constant for 60, 70 and 80 °C. Contrarily, a decrease is observed at the low current density conditions, when the operating temperature of the cell is 85 °C. Moreover, a decrease in the OCVs is observed for increasing cell temperature as shown in Fig. 7. Since the reaction rate increases as temperature increases, the decrease of the OCV and the low current performance are caused by hydrogen crossover. The electric and ionic resistance of the cell cause ohmic polarization in the higher current parts of the polarization curve as can be seen in Fig. 5. The numerical values calculated from the slope of the linear part of the curves are given in Fig. 7. The overall internal resistances of the cells constructed with sPS membranes are 0.86, 0.77, 0.87 and 0.88 Ω for the cell operating temperatures of 60, 70, 80 and 85 °C, respectively. Since the same cell, electrodes are used and the electrical resistance change is negligible at the related temperatures, the resistance change is due to the change in the ionic transport. It is found that cell resistance decreases up to 70 °C, and then increases for the further temperature increase. The maximum powers reached for the cells constructed with sPS membranes are 0.18, 0.20, 0.17 and 0.16 W/cm<sup>2</sup> for the cell operating temperatures 60, 70, 80 and 85 °C, respectively. This behavior has been explained by considering



**Fig. 7 – The comparison of the change of open circuit voltage (OCV) and cell resistance of the sulfonated polysulfone sPS (40% sulfonation) and sPS/TiO<sub>2</sub> composite membranes at different temperatures.**

excessive swelling at temperatures greater than 70 °C. That produces a deformation of the proton conduction channels with the consequent collapse of the membrane structure, causing a decrease in the fuel cell performance. Addition of TiO<sub>2</sub> to sPS (present work) or zeolite to SPEEK [35,12] increases the thermal stability of the composite membranes. TiO<sub>2</sub> or zeolite acts both as a mechanical reinforcement and keeping the water necessary to proton conduction. Therefore, the overall cell resistance decreases by increasing the temperature above 70 °C–85 °C. The resistance increases above 90 °C (data not given).

Analyzing the low current density behavior of the MEA prepared with sPS/TiO<sub>2</sub> membrane we see that the temperature increase results in a potential increase, as seen in Fig. 6. Moreover, the same OCV (0.96 V) is observed for increasing cell temperature from 70 °C to 85 °C, as shown in Fig. 7. Both of these results indicate that the addition of TiO<sub>2</sub> to sPS membrane reduces hydrogen crossover through the membrane at higher temperatures (80 °C and 85 °C). Another positive effect of the TiO<sub>2</sub> is the reduction of the ionic resistance. In Fig. 7 it is seen that the overall internal resistances of the cells constructed with sPS/TiO<sub>2</sub> membranes are 0.78 Ω, 0.70 Ω, and 0.65 Ω for the cell operating temperatures of 70 °C, 80 °C and 85 °C, respectively. The resistances obtained for the sPS/TiO<sub>2</sub> and sPS membranes are about the same at 70 °C. However, for 80 and 85 °C, the resistances of the cell constructed with sPS/TiO<sub>2</sub> composite membrane are 20% and 26% lower than the cell constructed with sPS membrane. The maximum power reached for the cell constructed with sPS/TiO<sub>2</sub> composite membranes is 0.20, 0.22 and 0.24 W/cm<sup>2</sup> for the cell operating temperatures of 70, 80 and 85 °C, respectively. The maximum power density measured for the cell constructed with sPS/TiO<sub>2</sub> composite membrane is 50% more than the cell constructed with sPS membrane operating at 85 °C.

#### 4. Conclusion

In this work, we investigated proton conducting polymer composite membranes based on sPS/TiO<sub>2</sub>.

PS was successfully sulfonated by the post-sulfonation method developed in the present work. The degree of sulfonation was controlled by varying the molar ratio of polymer to sulfonating agent. <sup>1</sup>H NMR, FTIR and elemental analysis results proved that the sulfonate groups were indeed quantitatively introduced into the polymers as expected. Composite membranes were prepared using DMAC as the casting solvent and TiO<sub>2</sub> as the inorganic filler. The membranes were characterized using XRD, TGA, water uptake, proton conductivity, and single cell performance. TGA results showed that the composite membranes have good thermal properties. The introduction of the inorganic filler supplies the composite membrane with a good thermal resistance and improves the water uptake.

Single fuel cell tests performed at different operating temperatures indicated that sPS/TiO<sub>2</sub> composite membrane is more stable hydrodynamically and also performed better than sPS membranes. Membrane electrode assemblies (MEAs) were prepared by gas diffusion layer (GDL) spraying method. The

maximum power reached for the cells constructed with sPS membranes is 0.18, 0.20, 0.17 and 0.16 W/cm<sup>2</sup> for the cell operating temperatures of 60, 70, 80 and 85 °C, respectively. The maximum power reached for the cell constructed with sPS/TiO<sub>2</sub> composite membranes is 0.20, 0.22 and 0.24 W/cm<sup>2</sup> for the cell operating temperatures 70, 80 and 85 °C, respectively. The maximum power density measured for the cell constructed with sPS/TiO<sub>2</sub> composite membrane is 50% more than the cell constructed with sPS membrane operating at 85 °C. These results should be conducive to the preparation of membranes suitable for PEMFC. We believe that sPS/TiO<sub>2</sub> composite membranes have good prospects for use in PEMFC.

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