

Polymer electrolytes based on sulfonated polysulfone for direct methanol fuel cells

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Abstract

This paper reports the development and characterization of sulfonated polysulfone (SPSf) polymer electrolytes for direct methanol fuel cells. The synthesis of sulfonated polysulfone was performed by a post sulfonation method using trimethyl silyl chlorosulfonate as a mild sulfonating agent. Bare polysulfone membranes were prepared with two different sulfonation levels (60%, SPSf-60 and 70%, SPSf-70), whereas, a composite membrane of SPSf-60 was prepared with 5 wt% silica filler. These membranes were investigated in direct methanol fuel cells (DMFCs) operating at low (30–40 °C) and high temperatures (100–120 °C). DMFC power densities were about 140 mW cm⁻² at 100 °C with the bare SPSf-60 membrane and 180 mW cm⁻² at 120 °C with the SPSf-60-SiO₂ composite membrane. The best performance achieved at ambient temperature using a membrane with high degree of sulfonation (70%, SPSf-70) was 20 mW cm⁻² at atmospheric pressure. This makes the polysulfone-based DMFC suitable for application in portable devices.

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1. Introduction

Low temperature fuel cells are emerging technologies for the electrochemical conversion of the chemical energy of a fuel into electric energy with low environmental impact and high energy efficiency. Nevertheless, before that these technologies could reach a full scale production, some problems have to be solved such as the high cost of fuel cell systems, their short term stability, etc. In an entire fuel cell system, significant costs are associated with noble metal catalyst and the commonly used perfluorosulfonate polymer electrolyte membrane. Up to now, the Nafion-type polymer electrolyte, a perfluorosulfonic acid polymer produced by DuPont, is the most widely used polymer electrolyte in H₂/air and direct methanol fuel cells for its high proton conductivity, excellent mechanical and thermal properties and, high chemical and electrochemical stability. However, the Nafion-type membrane also exhibits some negative aspects such as: high H₂ and methanol crossover, fast dehydration with

loss of proton conductivity at temperature above 100 °C, loss of fluorine ion in the exhaust gas due to •OH radicals attack. As a consequence, there are many research efforts addressed to the development of alternative membranes, which should be cheaper than Nafion and with similar or higher conductivity and lower fuel cross-over in the temperature ranges from 100 to 150 °C. The alternative polymeric membranes, currently investigated in fuel cells, are prepared from thermostable aromatic polymers such as sulfonated polyethersulfones [1–3], sulfonated polysulfones [4–6], sulfonated polyetherketones [7–9], sulfonated polyimide [10,11] and sulfonated polybenzimidazole (PBI) [12,13] and acid doped PBI [14,15]. The most frequent approach used for the synthesis of these polymer electrolytes, i.e. polymers with sulfonic groups in the backbone, consists of a post sulfonation method performed on available bare polymers, or by the sulfonation of monomers and subsequent copolymerization of sulfonated monomers. Among the aforementioned developed materials, the sulfonated polysulfone is one of the most promising for its low cost, the large commercial availability and its easy processability. For this reason, many research groups [5,6,16], including our own [4,17], are currently investigating these membranes for their application in low temperature fuel cells. To

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date, various details about synthesis [4–6], physico-chemical [4–6,18,19] characterization as well as proton conductivity, H₂/air [5,17,20] fuel cells performance can be found in the current literature. However, only in a few papers [16,21], the application of these membranes in high temperature (120 °C) direct methanol fuel cells has been reported. In this paper, the synthesis and characterization of sulfonated polysulfone with different degrees of sulfonation as well as preparation of composite polysulfone-based membranes for application in DMFC are presented. The assessment of such membranes has been made in a wide range of temperatures.

The sulfonated polysulfone (SPSf) was synthesized by a post sulfonation method using trimethyl silyl chlorosulfonate as a mild sulfonating agent in homogeneous solution of chloroform. This sulfonating agent was selected because it allows preserving the backbone structure from degradation phenomena such as cleavage of polymer chains, cross-linking and side reactions. A composite membrane based on silica and SPSf was also prepared and characterized for DMFC to extend the operating temperature up to 120 °C.

2. Experimental

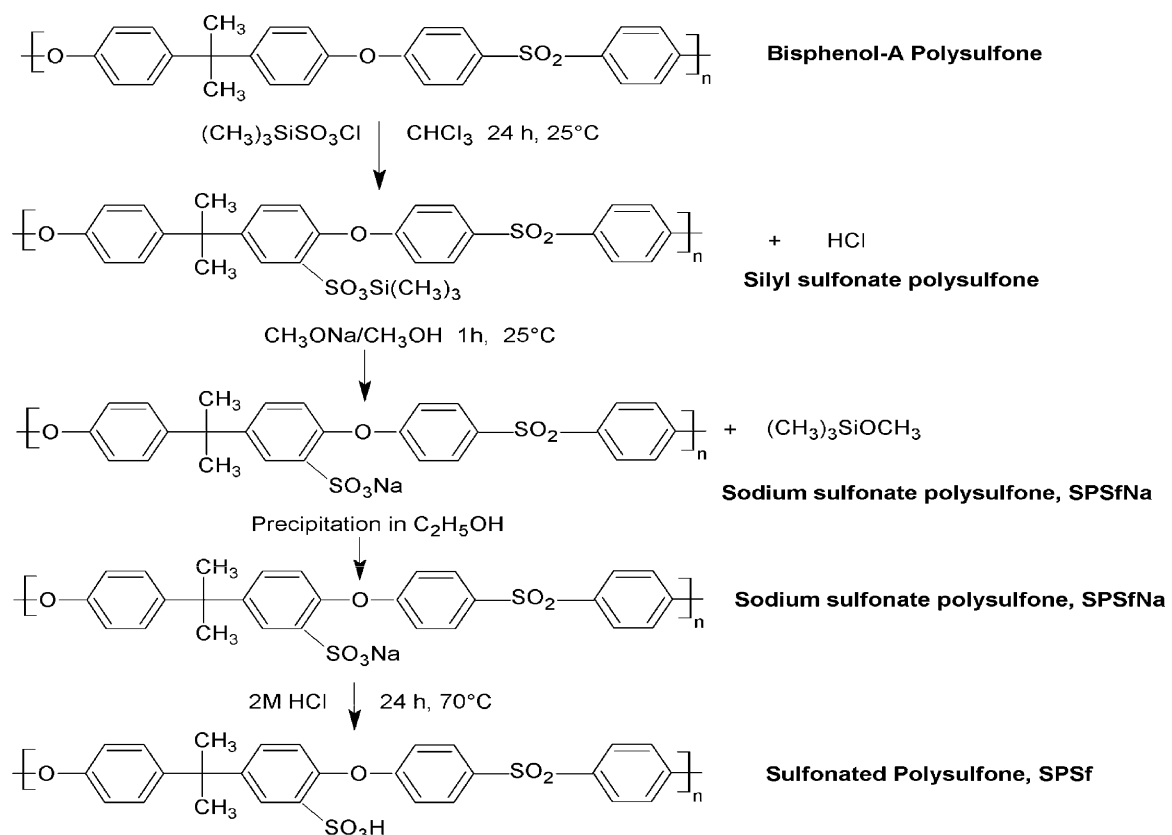
2.1. Synthesis of SPSf and membrane preparation

Scheme 1 shows the different steps for the procedure of synthesis. The commercial polysulfone Udel (Amoco) was dissolved in chloroform at a temperature of 25 °C and subsequently

treated with trimethylsilyl chlorosulfonate (Aldrich) to produce a silyl sulfonate polysulfone. The amount of intermediate product was controlled by the molar ratio of the sulfonating agent to the polymer repeating unit and varied from 2 to 2.3. The reaction time was 24 h at a temperature of 25 ± 0.1 °C. The obtained silyl sulfonate polysulfone polymer was then treated with a 30 wt% sodium methoxide/methanol solution (2.26 mmol per gram of polysulfone) at 25 °C for 1 h, which was used to cleave the silyl sulfonate moieties, yielding the sodium sulfonated polysulfone. The polymer was recovered by precipitation with ethanol. The precipitate was separated from mother liquor by filtration, vigorously washed with ethanol, and rinsed several times with distilled water. Finally, the sulfonated polysulfone powders were dried in an oven for at least 48 h at 110 °C for complete removal of solvents.

2.2. Preparation of membranes

The obtained SPSfNa polymer powders were dissolved in (0.5–1 g) in 5–10 ml of *N,N*-dimethylacetamide (DMAc) at ambient temperature to form a homogeneous solution. The membrane was afterwards prepared by casting the SPSfNa solution on a glass plate and the solvent was slowly evaporated at a temperature of 50 °C for at least 15 h. Subsequently, the membrane was peeled out from the glass with aid of distilled water, and then dried in oven at 80 °C under vacuum for at least 24 h. The membranes had thicknesses of about 80 μm in dry state. For some specific purposes, membranes of 150 μm were also



Scheme 1. Synthesis of sulfonated polysulfone.

Table 1
Characteristics of sulfonated polymer samples

Sample	X ^a	Level of sulfonation (%)	IEC by titration (meq g ⁻¹)	Water uptake (%)		2 M CH ₃ OH uptake (%)		Swelling ratio water (%)		Swelling ratio 2 M CH ₃ OH (%)	
				25 °C	80 °C	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SPSf-60	2.0	60	1.41	24.3	29.1	25.7	38.7	4.6	5.9	4.9	10.4
SPSf-70	2.3	70	1.42	32.5	–	31.9	–	6.3	–	6.2	–
^b SPSf-60-SiO ₂	2.0	60	1.35	24.3	28.9	25.3	38.2	4.8	6.2	5.1	10.6

Note: X^a = molar ratio of sulfonating agent to polymer repeating unit. Reaction time 24 h at 25 °C.

^bSPSf-60-SiO₂ = (SPSf-60 + 5 wt% SiO₂).

prepared. Finally, the membranes were converted into the acid form by treatment with 1 M HCl solution at 50–60 °C for 15 h and subsequently rinsed with water several times.

Composite membranes with a silica content of 5 wt% in SPSf-60 were prepared by using the following procedure. SPSfNa (0.5 g) was dissolved in 5 ml DMAc; silica (0.025 g of Cab-O-Sil, EH-5, particle size = 7 nm, by Cabot Corporation, Boston USA) was added to the solution, which was treated in an ultrasonic bath for 20 min. This solution was cast on a glass plate by a film applicator. The membranes, peeled out from glass, were dried at 80 °C under vacuum to remove traces of the solvent. The thickness of membranes was about 70–80 μm. The composite membranes were treated with HCl 1 M and then washed with distilled water. The characteristics of sulfonated polysulfone samples are listed in Table 1.

2.3. Physico-chemical characterization of PSf and sPSf samples

The as-prepared membranes were characterized by different techniques.

Elemental analyses were carried out with a Carlo Erba CHNS-O Analyzer model EA 1108 (Carlo-Erba, Milan, Italy).

Ion-exchange capacities (IECs) were determined by titration. A known amount of dry polymer (0.4–1.0 g) in acid form (after exchange in 1 M HCl at 80 °C for ~6 h) was suspended in 100 ml of 0.5 M NaCl solution under continuous stirring for ~18 h at 50–60 °C (see Table 1). The released amount of H⁺ was then determined by titration with a 0.1 M NaOH solution using phenolphthalein as indicator.

Thermal analysis of the sulfonated polysulfone membranes was studied by thermogravimetry (TGA) and differential scanning calorimetry (DSC). All measurements were performed by a Netzsch model STA 409 thermal analyzer in air in the temperature range from room temperature to 950 °C and with a heating rate of 5 °C min⁻¹.

The water/2 M MeOH uptake and swelling of membranes were obtained by measuring the change in weight and length between dry and wet conditions. Membranes of about 4 cm × 4 cm and with thickness of about 150 μm were used for these measurements. Prior to swelling/uptake measurements, the SPSf and composite membranes were dried at 80 °C under vacuum for at least 18 h. Then the membranes were immersed in water or 2 M MeOH at 25 °C for 24 h and/or at 80 °C for 2 h, and then wiped dry and quickly weighed/measured (length) again. The amount of uptake (wt%) and linear expansion (L%) were obtained using the equations: $wt\% = (wt_{wet} - wt_{dry})/wt_{dry} \times 100$; $L\% = (L_{wet} - L_{dry})/L_{dry} \times 100$; where wt_{wet} and wt_{dry} are the weights of the wet and dry membranes, respectively; while L_{wet} and L_{dry} are the length of the wet and dry membranes, respectively.

The surface and the cross-sectional morphologies of bare SPSf and composite membranes were investigated with a Philips XL30 scanning electron microscopy. The SEM observations were performed on samples coated with a thin sputtered layer of Au.

Table 2
Composition of MEA

MEA	Pt loading (mg cm^{-2})	Catalyst	Nafion loading in electrodes (wt%)
Anode	2.0	(60% PtRu (1:1)/Vulcan XC-72, E-Tek)	33
Cathode	2.0	(30% Pt/Vulcan XC-72, E-Tek)	33

2.4. DMFC performance and cell resistance measurements

The thickness of SPSf membranes used in the experiments was about 80 μm .

Direct methanol fuel cell measurements were performed in single cell using an aqueous solution of 2 M methanol as fuel and oxygen as oxidant. The anode catalyst was a 60 wt% Pt-Ru (1:1)/Vulcan (E-TEK), whereas the cathode was a 30 wt% Pt/Vulcan (E-TEK). The platinum loading in all electrodes was $2 \pm 0.2 \text{ mg cm}^{-2}$. For both anode and cathode, the catalyst layer, consisting of 67 wt% catalyst and 33 wt% Nafion, was coated on carbon cloth covered with a diffusion layer (acetylene black and 20 wt% PTFE) (for details see also Table 2).

Membrane and electrodes assemblies (MEAs) were prepared by hot pressing the electrodes (anode and cathode) onto the sulfonated polysulfone or composite membranes at 130 °C and 50 kg cm^{-2} for 90 s. The MEAs were tested into a 5 cm^2 single cell (GlobeTech Inc.) connected to a HP 6060B electronic load. The methanol solution was fed at the anode at a flow rate of 2.5 ml min^{-1} ; whereas, oxygen was fed at cathode at a flow rate of 500 ml min^{-1} . Oxygen was passed before its introduction into the cell, through a humidification bottle maintained at 100 °C during operation with the SPSf-60 membrane and at 85 °C using the MEA based on the composite membrane. Different operating temperatures of the cell were settled in the range from 90 to 120 °C. The anode back-pressure varied from 1 to 2.5 atm abs., when the temperature was increased from 90 to 120 °C; the back-pressure of cathode compartment was maintained constant at 3.5 atm abs. The performance of each MEA was measured under steady-state conditions. The cell resistance measurements (proton conductivity) were determined in the 5 cm^2 single cell during start-up and fuel cell operation by an impedance bridge and by a current interruption method, respectively. Electrochemical characterizations of a SPSf-70 membrane in 2 M MeOH/O₂ were also performed at atmospheric pressure and temperatures from 29 to 40 °C. In a second set of measurements at temperatures from 40 to 90 °C, ambient pressure was used for the anode compartment (2 M methanol) and 3.5 atm abs for the cathode compartment.

3. Results

3.1. Synthesis and physico-chemical characteristics of membranes

Two samples of sulfonated polysulfone membranes, named SPSf-60 and SPSf-70, and a composite membrane, SPSf60-SiO₂ were prepared. For all the samples, the sulfonation levels, the ion exchange capacity (IEC) as well as their water and methanol uptake/swelling, measured at 25 and 80 °C, are

reported in Table 1. The degree of sulfonation for the studied samples varied from 60 to 70 wt% as calculated by elemental analysis. The water uptake for SPSf-60 and SPSf60-SiO₂ membrane was ranging from 24 to 29 wt% at 25 and 80 °C; whereas, a high 2 M MeOH uptake of $38 \pm 1 \text{ wt}\%$ was found at 80 °C. The other sample, SPSf-70, showed higher water/methanol uptake of about 32 wt% at 25 °C. The degree of swelling was found significantly smaller than that of the solution uptake for all membranes. It varied from 4% to 6% at 25 °C; whereas, these values rose up to 10% upon the swelling in 2 M MeOH at 80 °C (Table 1).

3.1.1. Thermal analysis

Fig. 1 shows the thermal properties for the bare polysulfone and for a sulfonated polysulfone sample. The DSC curves (inset in Fig. 1) show an increase in glass transition temperature from 187 °C for the bare polysulfone to about 205 °C for the sulfonated polysulfone. Moreover, an increase in glass transition temperature (T_g) with the increasing degree of sulfonation of the polymer is observed, which is in agreement with the results reported in the literature [17,22]. The upper limit of thermal stability of these materials, as shown by TGA curves, should be up to 220–250 °C [16,17,19,22], after which, the desulfonation process starts. From the inset of Fig. 1, it is also found that the desulfonation peak for the composite membrane (SPSf60-SiO₂) compared to SPSf-60 membrane is increased from 234 to 242 °C. This is attributed to the interaction of silica particles with the polymer matrix producing a slight increase of its thermal stability. An accurate study on thermal stability of SPSf membranes was recently carried out by Park et al. [22]; thermal properties were investigated using thermogravimetric analysis/mass spectrometry (TGA–MS). They found that the evolution of SO₂ and SO gases due to desulfonation process started at temperatures higher than 200 °C [22]. Similar findings were also reported in previous studies [17,23] performed on non-perfluorinated and

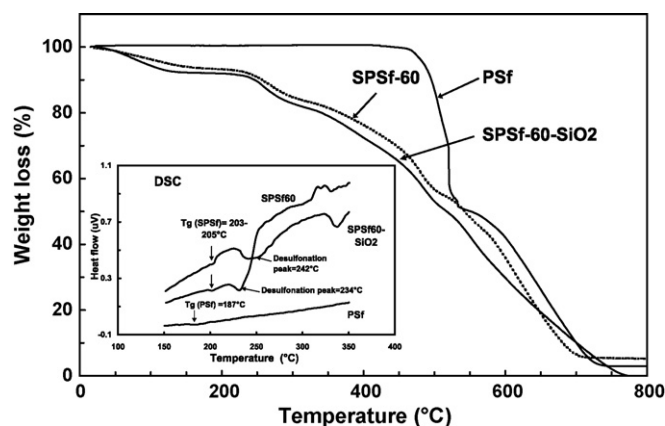


Fig. 1. TGA and DSC thermograms of polysulfone membranes.

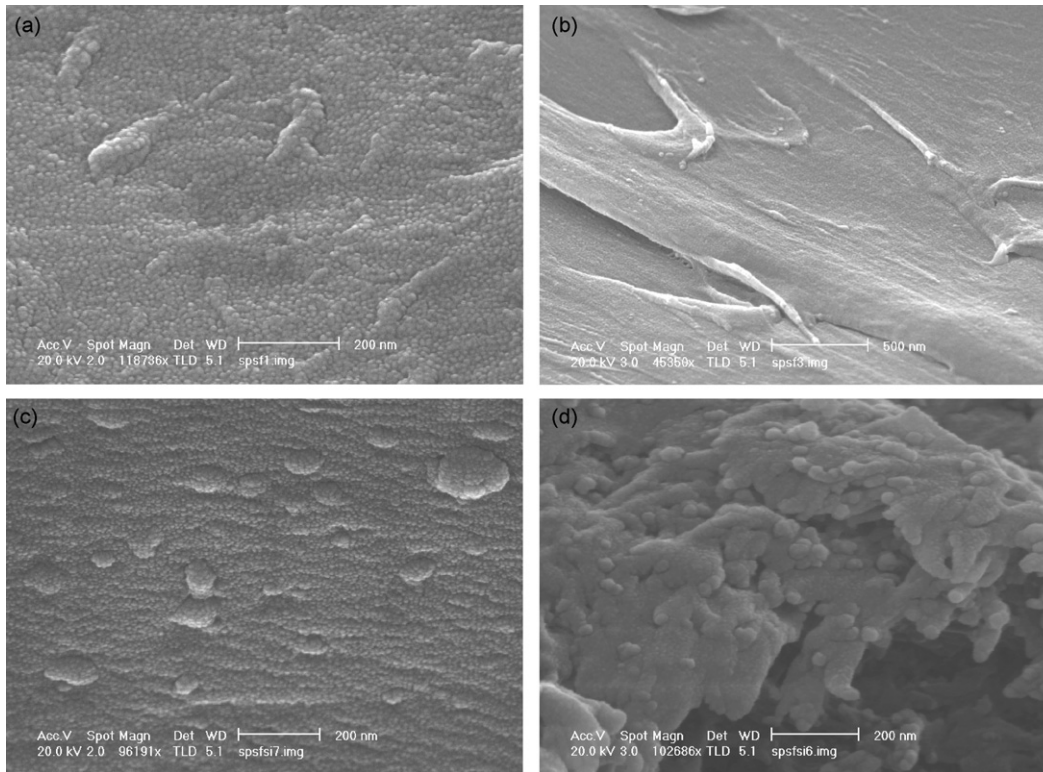


Fig. 2. SEM images of surface and cross-sectional morphology for SPSf-60 (a, b) and SPSf-60-SiO₂ (c, d) membranes.

perfluorosulfonate ionomers. Thus, the temperature of about 200 °C represents the starting point of desulfonation for this type of ionomeric polymer. However, such phenomena could appear at temperature slightly different than 200 °C, in dependence of the polymer structure and/or the presence in the bare polymer of side groups. These can mask the starting process of desulfonation or even accelerate it, as a function of the environment (type of gas, heating rate, etc.) in which it occurs. Therefore, with a reasonably good approximation, a practical fuel cell temperature up to 150–160 °C for this type of ionomeric polymers could be possible. It is known that the performance of the membranes in H₂/air and methanol/air fuel cells depend on the mechanical, chemical and electrochemical stability, as well as their capability to maintain high proton conductivity and good lifetime for DMFC performance under temperatures higher than 100 °C.

3.1.2. Morphology studies

The surface morphology of the dried membranes was investigated using SEM. Fig. 2 shows the scanning electron micrographs of the SPSf-60 membrane (Fig. 2a and b) and of SPSf-60-SiO₂ composite membrane (Fig. 2c and d). The surface and cross-sectional images show the dense structure of the SPSf-60 membrane (Fig. 2a and b) and, moreover, an evidence of the thin gold film sputtered on the top of membrane surface. The composite membrane showed a relatively uniform distribution of silica particles in the polymer matrix (see Fig. 2c and d). However, from images it is possible to observe the agglomeration of silica particles because their dimensions are in the range

of 20–50 nm, which are higher than their average particle size of 7 nm for primary particles.

3.2. Fuel cell performance of SPSf-60 and SPSf-60-SiO₂ membranes

Fig. 3 shows the DMFC performances at 90 and 100 °C for the cell equipped with sulfonated polysulfone membrane, SPSf-60. The fuel cell performance at 100 °C compared to 90 °C shows lower OCV (0.77 vs. 0.85 V), but higher power density (~140 vs. ~120 mW cm⁻²). During DMFC measurements, a further increase in cell temperature produced a decrease in cell performance and an unstable behavior, due to dehydration of the

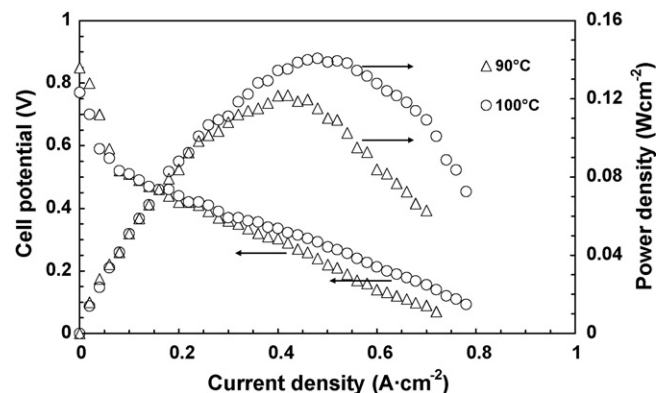


Fig. 3. Polarization and power density curves for a cell equipped with sulfonated polysulfone, SPSf-60 at 90 °C and 100 °C in 2 M MeOH/O₂.

membrane under these conditions. It is well known that it is possible to increase fuel cell temperature in direct methanol fuel cells using composite membranes, which present better water retention under temperatures above 100 °C [24,25]. However, when the fuel cell temperature is raised, the methanol cross-over through the membrane increases, but there is also an enhancement of methanol electro-oxidation kinetics. The fuel cross-over decreases the open circuit voltage (OCV) due to the presence of a mixed potential at the cathode, whereas improved electrokinetics are generally associated with higher power densities. Thus, the negative effect of increased methanol crossover is counterbalanced by a decrease of the activation energy of the methanol electro-oxidation reaction. Polarization experiments at different temperatures (from 90 to 120 °C) were performed on the cell equipped with the composite membrane (SPSf-60-SiO₂). Two representative DMFC performances obtained at 100 and 120 °C are reported in the Fig. 4. The maximum power density for the cell with the composite membrane at 100 °C is $\sim 140 \text{ mW cm}^{-2}$, which is practically the same than that obtained with the bare sulfonated polysulfone membrane at the same temperature. However, a higher fuel cell performance, with a maximum power density of 180 mW cm^{-2} was achieved at 120 °C with the SPSf-60-SiO₂ composite membrane.

A direct comparison of the present results with those obtained with other non-perfluorinated ionomer membranes on the basis of the current literature is not easy, since generally the physicochemical and electrochemical characteristics of the sulfonated ionomers are different. Moreover, it is difficult to compare fuel cell performance, when different kinds of catalysts (supported or unsupported) and various noble metal loadings (mg cm^{-2}) are used as well as when the DMFC measurements are performed at different pressures and temperatures. As examples of DMFC performance obtained with non-perfluorinated membranes, Fu and Manthiram [16] reported power densities of about $40\text{--}50 \text{ mW cm}^{-2}$ with a sulfonated polysulfone membrane, SPSf, at 80 °C in 2 M MeOH/O₂ and with a catalyst loading of 0.6 mg cm^{-2} of Pt-Ru/C at anode and 1 mg cm^{-2} of Pt/C at cathode. Kim et al. [26] showed power densities of about 120 mW cm^{-2} at 90 °C with disulfonated poly(arylene

ether benzonitrile) (6FCN-35) copolymers in 0.5 M MeOH/air and with catalyst loading of 10 mg cm^{-2} of unsupported Pt-Ru at anode and 6 mg cm^{-2} of unsupported Pt at cathode. Li et al. [28] reported power density of 110 mW cm^{-2} at 70 °C with a sulfonated poly(ether ether ketone) membrane in 2 M MeOH/O₂ and with catalyst loading of 2.5 mg cm^{-2} of Pt-Ru/C at anode and 2.5 mg cm^{-2} of Pt/C at cathode. Silva et al. [27] showed power densities of 50 mW cm^{-2} at 130 °C with a composite sulfonated poly(ether ether ketone) membrane, SPEEK-ZrPh-PBI, in 1.5 M MeOH/O₂ and with catalyst loading of 1 mg cm^{-2} of Pt-Ru/C at anode and 0.4 mg cm^{-2} of Pt/C at cathode. Further details on these and other types of membranes including the composite membranes proposed for fuel cell applications can be found in literature reviews [29–32].

Moreover, a general advantage of SPSf membranes compared to Nafion-type membranes is that the non-perfluorinated membranes exhibit lower methanol cross-over. Although, we did not carry out specific methanol permeability measurements, it is well known from the current literature that these materials have a MeOH permeability at least one order of magnitude lower than Nafion-type membranes [16,26–28]. Although, the polysulfone membranes with the same level of sulfonation of Nafion-based membranes show lower proton conductivity, such a drawback can be compensated by a decrease of its thickness, being low the methanol cross-over.

3.3. Cell resistance measurements

Fig. 5 shows the cell resistance values as a function of the temperature measured during the start up and during operation of the cell equipped with the SPSf-60 and composite (SPSf-60-SiO₂) membranes, respectively. At temperatures lower than 60 °C, a high membrane resistance was observed, which could be due to its slow re-hydration after the drying effect caused by the hot pressing procedure for MEA fabrication. Cell resistance measurements at temperatures up to 90 °C were performed by using an impedance bridge [33], whereas at higher temperatures these measurements were carried out by using a digital oscilloscope and the current interruption method [17,33]. In the latter case, the cell resistance is quite small not only due to the increased

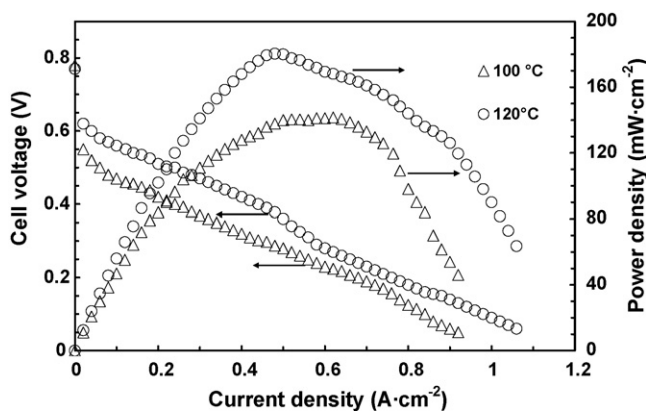


Fig. 4. Cell voltage and power density as a function of current density for the SPSf-60-SiO₂ membrane-based DMFC at temperatures of 100 and 120 °C in 2 M MeOH/O₂.

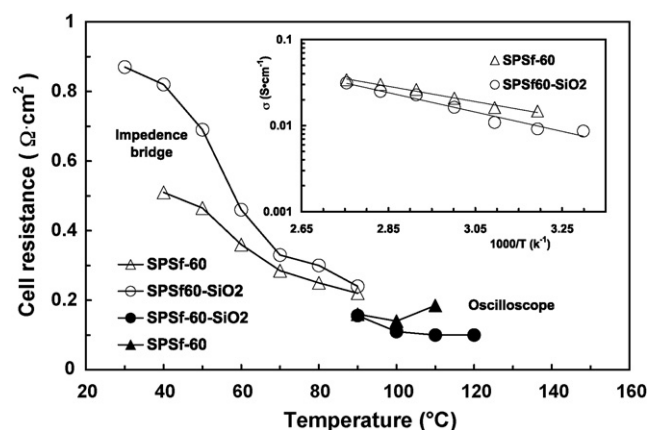


Fig. 5. Cell resistance and proton conductivity of SPSf-60 and SPSf-60-SiO₂ membranes as a function of the temperature.

temperature but also as consequence of improved internal humidification due to the water produced at the cathode during normal fuel cell operation. At temperatures lower than 90 °C, the cell resistance of bare SPSf-60 membrane is lower than that of the composite SPSf-60-SiO₂, whereas at $T > 100$ °C there is an inversion and the composite membrane became less resistive. This may indicate that the water retention of the composite membrane at higher temperature ($T > 100$ °C) is greater than that of bare SPSf membrane. A comparison of values of proton conductivity for the two membranes as measured by impedance bridge is reported in the inset of Fig. 5. The two membranes show different conductivities at lower temperature than 80 °C, while at 90 °C, the two samples reach the same level of about $3.2 \times 10^{-2} \text{ S cm}^{-1}$. Moreover, the behavior of proton conductivity for the studied membranes is typical of thermally activated process. The calculation of activation energy derived from the slope of $\log \sigma$ vs. $1/T$ plots give values of 17 and 21.6 kJ mol⁻¹ for SPSf-60 and SPSf-60-SiO₂ membranes, respectively. From the analysis of Fig. 5, it appears that the cell resistance reaches a value as low as $\sim 0.1 \Omega \text{ cm}^2$ ($\sigma = 7.5 \times 10^{-2} \text{ S cm}^{-1}$) under temperatures of 100–120 °C. This value is comparable to that usually reported with various types of membranes investigated in DMFCs [26–28,33].

3.4. DMFC performance at ambient temperature

As discussed above the DMFC performance with sulfonated polysulfone membranes has been reported in a few papers [16,21]; yet, limited attention was devoted to the investigation of the behavior of these membranes in DMFCs under conditions near at ambient temperature. Studies at ambient temperature are interesting because the DMFCs are promising devices to replace secondary batteries in portable applications. In order to investigate the low temperature behavior of polysulfone-based DMFC, a membrane with 70% of sulfonation (SPSf-70) has been used for these experiments. Fig. 6 shows the polarization and the power density curves at different temperatures (from 29 to 40 °C). Methanol and oxygen are fed in the cell at atmospheric pressure to simulate conditions close to those in portable applications. Due to the poor catalytic activity towards the methanol

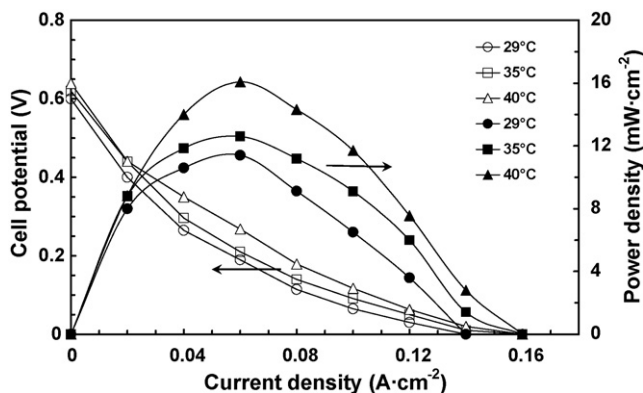


Fig. 6. Cell voltage and power density as a function of current density for the SPSf-70 membrane at ambient temperatures from 29 to 40 °C and at atmospheric pressure.

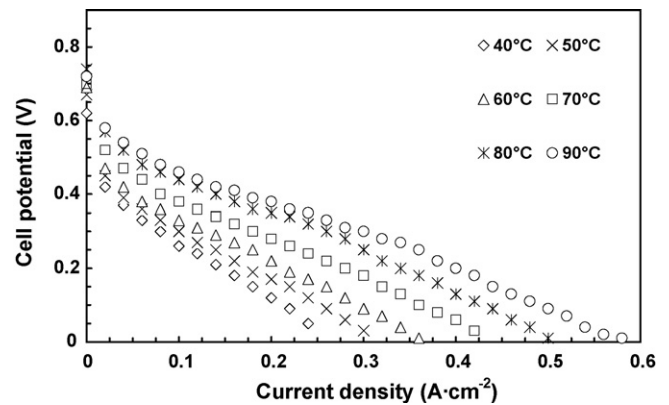


Fig. 7. Cell polarization for the SPSf-70 membrane-based DMFC at different temperatures from 40 to 90 °C at atmospheric pressure of MeOH and with O₂ at 3.5 bar abs.

electro-oxidation at ambient temperature and to the low partial pressure of oxygen, the OCV of the cell is rather low if compared to that reported in Figs. 3 and 4. However, the OCV increases with the temperature from 0.62 V at 29 °C to 0.65 V at 40 °C. Also the power density increases with the temperature from $\sim 11 \text{ mW cm}^{-2}$ at 29 °C up to about 16 mW cm^{-2} at 40 °C. A more remarkable improvement of electrochemical performance has been obtained by increasing the oxygen pressure at cathode. Fig. 7 shows the polarization curves for temperatures varying from 40 to 90 °C with methanol fuel fed at atmospheric pressure and oxygen fed at 3.5 atm abs. The increase of partial pressure of oxygen produces an increase of the OCV as well as of the cell performance. Fig. 8 shows the same trend for the power density, with the increase of temperature. A value of 30 mW cm^{-2} at 40 °C is recorded, while a higher power density of 95 mW cm^{-2} is obtained at 90 °C. These fuel cell performances at near ambient temperature are competing with those reported in the current literature for DMFCs [34–36]. Very recently, Wee [34] has reviewed the research activities in DMFCs for portable devices, and has evidenced that delivered power densities are generally within the range from 20 to 50 mW cm^{-2} for DMFC with 1–2 M MeOH as fuel at a temperature of 60 °C and at atmospheric pressure. However, power densities of $60\text{--}100 \text{ mW cm}^{-2}$ at 60 °C

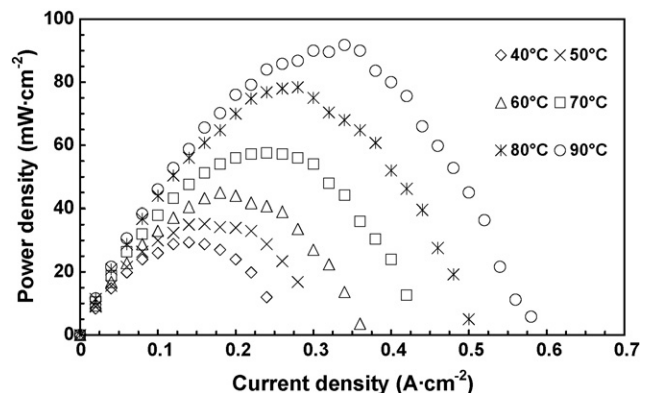


Fig. 8. Power density curves for the SPSf-70 membrane at different temperatures from 40 to 90 °C at atmospheric pressure of MeOH and with O₂ at 3.5 bar abs.

have been recently reported for Nafion-based direct methanol fuel cells [35,36].

Therefore, the performances achieved in the present work are interesting and represent a good starting point for further development of sulfonated polysulfone membrane. It is observed that the electrodes used in these experiments are of standard type with Nafion ionomer in the catalytic layer [33,37]; thus, further enhancement may be expected by optimizing the electrodes and MEA manufacturing for the polysulfone membranes. Other improvements concern with an accurate choice of the sulfonation level for the sulfonated polysulfone or by the use of suitable fillers for the polymers, which should improve the characteristics of these ionomer membranes for DMFCs.

4. Conclusion

The sulfonated polysulfone (SPSf) was successfully synthesized using a post sulfonation method and tested as polymer electrolyte membrane in direct methanol fuel cells. The thermal analysis measurements of SPSf show an increase in glass transition temperature (T_g) from 187 °C for the bare polysulfone to 205 °C for the sulfonated polymer. The introduction of bulky sulfonic groups in the polymer modifies the structure symmetry lowering the thermal stability of the material. Moreover, the thermograms reveal a possible desulfonation process in the range from 220 to 240 °C, which is related to the initial decomposition of the backbone structure of the polymer. A membrane of sulfonated polysulfone, SPSf-60, was successfully investigated in 2 M MeOH/O₂ fuel cells at temperatures up to 100 °C, whereas with the composite membrane, SPSf-60-SiO₂, a maximum operating temperature of 120 °C was reached and a power density of 180 mW cm⁻² was obtained. The latter result was likely due to an improved water retention capability of the composite membrane at high temperatures (100–120 °C). A low cell resistance of 0.1 Ω cm² was measured at these temperatures. Preliminary tests performed at ambient temperature with membranes characterized by a higher level of sulfonation, i.e. SPSf-70, showed power densities of about 15–20 mW cm⁻², which make them suitable for possible use in portable devices.

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