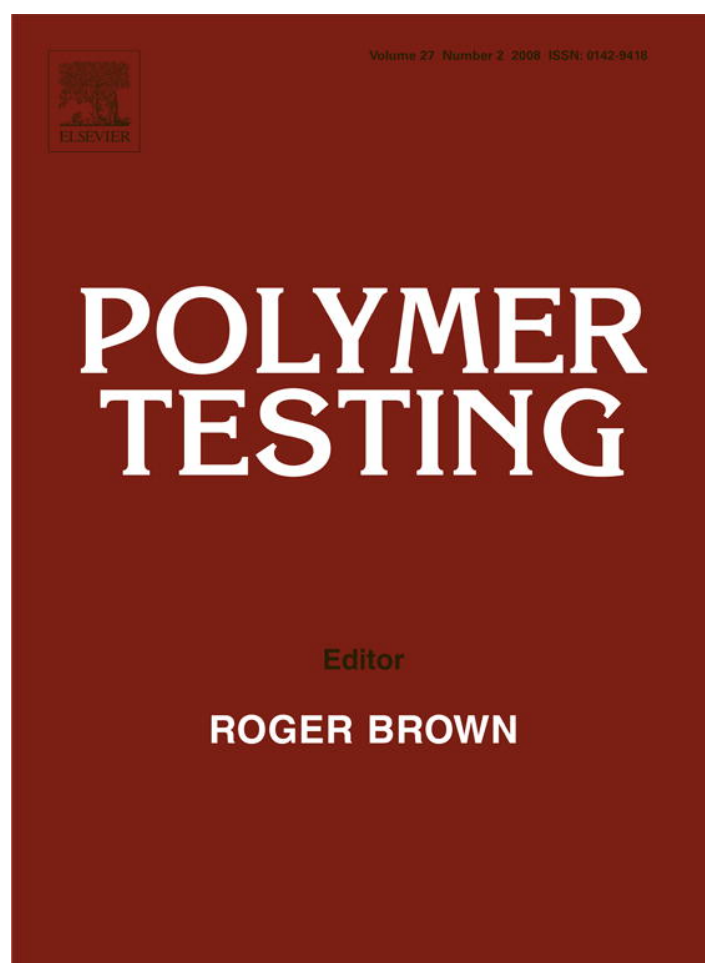


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Product Performance

Sulphonated polysulphone membranes for medium temperature in polymer electrolyte fuel cells (PEFC)

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Abstract

The synthesis of sulphonated polysulphone (PSF) with three different sulphonation levels was carried out and several membranes were developed with the corresponding polymers.

The membranes were characterised in terms of ion exchange capacity (IEC), water up-take at different temperatures, TG–DSC analysis, FT-IR investigation and methanol permeability measurements.

The results obtained were correlated to the electrochemical data. Electrochemical tests in a single cell fed with H₂/air were also carried out in the temperature range 80–120 °C and compared to commercial Nafion 112 (N112).

The chemical–physical properties of the tested membranes have good reproducibility and comparable values with commercial Nafion. A maximum power density of about 360 mW cm⁻² for PSF –48% at 0.6 V and *T* = 120 °C was obtained, and the measured OCV value for the PSF membrane is higher than the perfluorinated membrane with a comparable thickness, indicating a lower gas permeability of PSF polymer.

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Keywords: Sulphonated polysulphone; Membrane preparation; Physico-chemical characterisations; Polymer electrolyte fuel cells

1. Introduction

The technology of polymer electrolyte fuel cells (PEFCs) working at temperatures lower than 100 °C and using hydrogen as a fuel is well established [1].

The Nafion membranes are the most commonly used materials as a polymer electrolyte in these devices. They have chemical and physical properties suitable for the demanding fuel cell conditions, but this kind of membrane is expensive because

of the fluorochemistry involved in the synthesis. Moreover, the large-scale application of PEFC is limited not only by the high cost but also by the narrow range of operative temperatures.

The main problem is the Pt-based electrocatalyst poisoning by CO contained in the fuel when H₂ reformat is used. Taking into account that the adduct Pt–CO is thermolabile, a fuel cell working at a temperature of about 100–130 °C could drastically reduce or eliminate the poisoning and even allow platinum to be replaced by less expensive catalysts.

For these reasons, many studies have been carried out to provide cheaper and more thermostable membranes based on aromatic polymers

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such as polysulphones (PSF), polyethersulphones, polyetherketones, polyimides and polybenzimidazoles [2,3].

Among the above-mentioned polymers, PSF is considered to be very interesting due to its low cost and commercial availability [3–7]. Recently, some papers [8–10] on the application of so-called cardo PSFs or polyetersulphones for ion conducting membranes have appeared.

Two different procedures for PSF sulphonation are generally used. In one procedure, the sodium-sulphonated group was introduced into the PSF backbone via a metalation–sulfination–oxidation process [11], and in other one the trimethylsilyl chlorosulphonate was used as the sulphonating agent [12]. In the present work, this second functionalisation has been used.

The results on the preparation and characterisation of membranes based on a sulphonated PSF at different sulphonation levels, and also the physico-chemical and electrochemical properties, are reported.

2. Experimental

2.1. Synthesis of sulphonated PSF

The following procedure [13] was used to prepare the sulphonated PSF samples.

A commercial PSF Aldrich (M_n ca. 26,000, T_g 190 °C) was dried under vacuum in an oven at 140 °C for 4 h, and then dissolved in chloroform at 30 °C under stirring. Trimethylsilyl chlorosulphonate (Aldrich) was added, at the same temperature, to produce silyl sulphonate PSF intermediate and hydrochloric acid [12]. It is possible to act on three main parameters: temperature, time and molar ratio of the sulphonate agent/PSF to vary the degree of sulphonation (DS) of the polymer; in this work, we have maintained both the reaction temperature ($T = 30$ °C) and the molar ratio ($n = 2.3$) constant, varying the sulphonation time.

Successively, the sodium methoxide was added to the solution to cleave the silyl sulphonate intermediate and to obtain the final sulphonated sodium product, then the light pink sulphonated polymer was precipitated in cold isopropilic alcohol, washed, filtered and finally dried in an oven at 70 and 110 °C.

Three polymers were prepared with different sulphonation time: PSF-24 h, PSF-48 h and PSF-72 h [14].

2.2. Membranes preparation

Transparent membranes of sulphonated PSF were obtained by dissolving the polymer in *N,N*-dimethylacetamide (DMAc) at about 100 °C under stirring, to obtain a dispersion of 6% (wt/wt).

The solution was evaporated until reaching a suitable density to be stratified on a glass plate by the doctor-blade casting technique. By varying the knife-edge, this method allows scaled-up membranes with a good mechanical resistance and homogeneity of thickness to be prepared.

The obtained films were held at 70 °C for about 18 h [15] on the glass to evaporate the solvent. Then, the membranes were treated in distilled water to remove any residue of solvent and in 1 M hydrochloric acid solution for 18 h at 60 °C, and washed again to remove any residue of acids. This treatment was carried out to exchange Na^+ with H^+ ions.

Three membranes with different degrees of sulphonation were prepared: PSF-40%, PSF-48% and PSF-69%, with a thickness ranging between 60 and 85 μm .

2.3. Physico-chemical characterisations

The thermo gravimetric analysis (TG) was carried out with a Netzsch thermo balance (mod. STA 409) in air, following the variation of the percentage mass loss in weight, in the temperature range 20–1100 °C with an increase of 5 °C min^{-1} . The TG measurements were carried out both on the sodium and acid sulphonated PSF powder.

With the same equipment, differential thermal analysis (DTA) on sodium sulphonated PSF powders was carried out.

Differential scanning calorimetry (DSC) analyses were performed by a Perkin-Elmer Pyris 1 instrument in air, in the temperature range 50–250 °C with an increase of 20 °C min^{-1} (all the membranes were thermally treated before the measure, only the PSF Aldrich was in pellet form).

The water uptake measurement was determined by the difference in weight between the wet sample (m_{wet}) and the dry sample (m_{dry}).

The dry weight was obtained by treating the membranes in an oven at 80 °C under vacuum for 2 h while for the wet weight the same sample was immersed in water at room temperature for 24 h, and at 60, 80 and 100 °C for 2 h. The percentage of absorbed water from the membranes was calculated as follows:

$$wu\% = \left[\frac{m_{wet} - m_{dry}}{m_{dry}} \right] \times 100. \quad (1)$$

The ionic exchange capacity (IEC), expressed as moles of sulphonated polymer for 1 g of dry polymer, was determined through an acid-base titration using an automatic titrator (Metrhom Mod.751GPD Titrimo). After the weight determination in the dried form (m_{dry}), samples were immersed in a 1 M sodium chloride solution for 18 h at 60 °C in order to exchange H^+ ions of the polymer with Na^+ ions present in the solution. The solution was titrated with a 0.01 N sodium hydroxide solution. The equivalent volume (V_{eq}) was determined and the IEC calculated according to the equation:

$$\text{IEC} = \left[\frac{V_{\text{eq}}[\text{NaOH}]}{m_{\text{dry}}} \right], \quad (2)$$

where IEC is the ion exchange capacity expressed in meq g^{-1} ; V_{eq} is the added titrant volume at the equivalent point expressed in ml; $[\text{NaOH}]$ is the normal concentration of the titrant; m_{dry} is the dry mass of the sample expressed in g.

The membrane thickness was measured by using a thickness gauge (Mitutoyo Corp. Mod. ID-C112PB) after detaching the membrane from the glass plate.

The FT-IR analyses were carried out on Perkin-Elmer spectrum GX FT-IR spectrometer with Mirtgs Detector. All the membranes were tested by using the horizontal attenuated total reflectance (HATR) technique. All spectra were measured at room temperature and represent the average of 16 scans at a resolution of 4 cm^{-1} .

The methanol permeability of membranes was measured by using a home-made glass diffusion system at room temperature. This system consists of two compartments (Fig. 1), one compartment (A) was filled with the methanol solution 1 M, while the other flask (B) was filled with deionised water.

Both compartments were stirred continuously during the measurements. A methanol flux was established across the membrane owing to the concentration difference between the two compartments. At different times (15, 75, 180, 300 and 1440 min), the same amounts of solution were taken from the flask (B). The methanol concentration was detected by gas chromatography (Agilent Mod. 6890N).

The methanol concentration in flask (B) as a function of time is given by:

$$C_{\text{B}}(t) = \frac{A \times DK \times C_{\text{A}}(t - t_0)}{V_{\text{B}}L}, \quad (3)$$

where C_{A} and C_{B} are the concentrations of methanol in cells A and B, respectively. A represents the area of the membrane; L , the thickness and V_{B} , the volume of cell B. D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The product DK is the methanol permeability (P , $\text{cm}^2 \text{ s}^{-1}$), which can be directly determined by the slope of the plot of $(C_{\text{B}}(t)V_{\text{B}}L/AC_{\text{A}})$ versus time.

2.4. Electrochemical characterisations

The PSF-40%, PSF-48%, PSF-69% and commercial Nafion 112 membranes were assembled by hot-pressing between home-made standard electrodes with the same Pt loading (0.5 mg cm^{-2}) for anodes and cathodes in the catalyst layer and using a low PTFE content in the diffusion layer. 30% Pt/Vulcan (E-TEK Inc.) was used as an electrocatalyst. The electrode preparation procedure based on a spraying technique is described elsewhere [16].

The obtained MEAs were characterised in a 5 cm^2 commercial single cell.

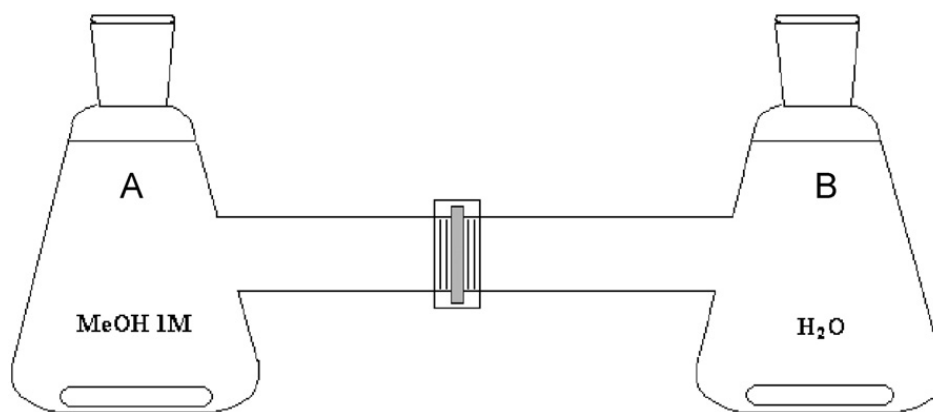


Fig. 1. Home-made glass diffusion system for methanol permeability measurements.

The gas fluxes were fixed at 1.5 times the stoichiometry for the fuel and twice the stoichiometric value for the oxidant at a current density of 1.0 A cm^{-2} .

MEAs were tested in the temperature range $80\text{--}120^\circ\text{C}$ in H_2/air , maintaining the gas humidifying temperature 10°C at the anode and 5°C at the cathode higher than the cell temperature at 3.0/3.0 abs. bar.

The polarisation curves were recorded by means of a test station equipped with software for automatic data acquisition, and the cell resistance was measured with an Agilent milliohmmeter by a static method at a frequency of 1 kHz.

3. Results and discussion

The degree of sulphonation of sulphonated PSF powders was obtained by thermal analysis. Fig. 2 shows the thermal profiles of the polymers in acid form (PSF-H).

It is possible to observe three distinct zones [17]: the mass loss at temperatures ranging from 30 to 150°C , corresponding to the loss of absorbed water coordinated to the sulphonic groups. In the temperature range of $240\text{--}330^\circ\text{C}$, the de-sulphonation process is evident; these mass losses increase by increasing the sulphonation degree. The last zone at temperatures over 330°C indicates the decomposition of the polymer main chain, which is completely burnt at about 800°C .

Fig. 3 reports the thermal profile of the polymers in sodium form (PSF-Na).

Even in this case, there is a mass loss in the temperature range of $30\text{--}150^\circ\text{C}$ attributable to the water loss coordinated to the sulphonic groups. The second mass loss is shifted to higher temperature ($280\text{--}390^\circ\text{C}$) than for acid form polymers, due to the presence of Na^+ ions that stabilise the polymer. Contrary to the acid form, these mass losses are the same for all polymers, while a difference, depending on the sulphonation degree, was highlighted at $T > 800^\circ\text{C}$. In fact, as is reported in Table 1, different residual masses were found at 900°C as a function of degree of sulphonation.

It was supposed that these residual masses could be due to Na_2SO_4 produced during the heating runs of TG analyses. This hypothesis was verified by a sulphate identification test and by monitoring the melting temperature during DTA analyses. An endothermic peak at about 800°C , corresponding to the typical melting point of Na_2SO_4 , was found and is reported in Fig. 4.

In the 1st column of Table 1, the mass loss in the temperature range of the de-sulphonation process is reported. The difference between the sulphonic groups loss percentage of acid and sodium forms is evident. In the 2nd column, the residual mass percentages of sodium form are listed and, in the 3rd column, the total percentages of both acid and sodium form are shown. In the last column, the degrees of sulphonation calculated from the total

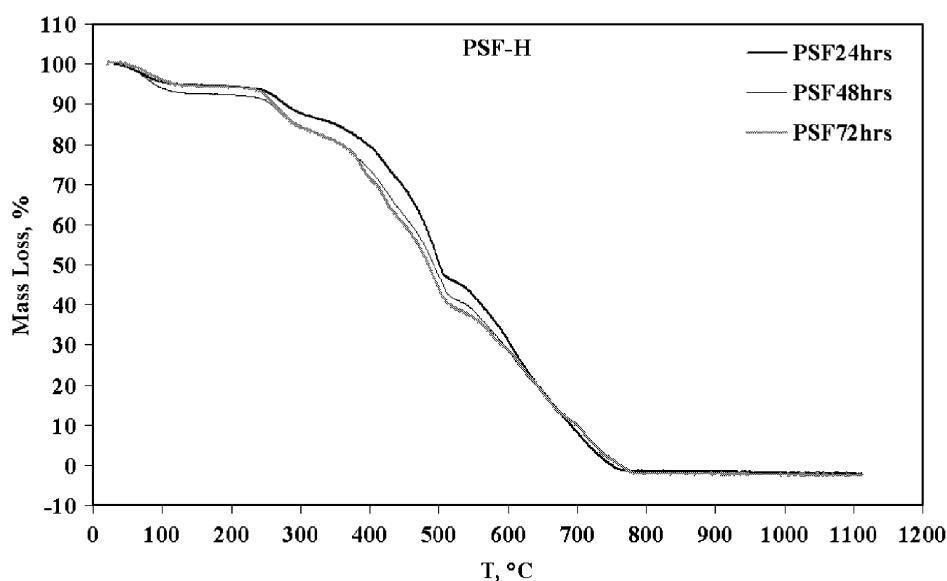


Fig. 2. TG analyses of sulphonated polysulphone powders in acid form.

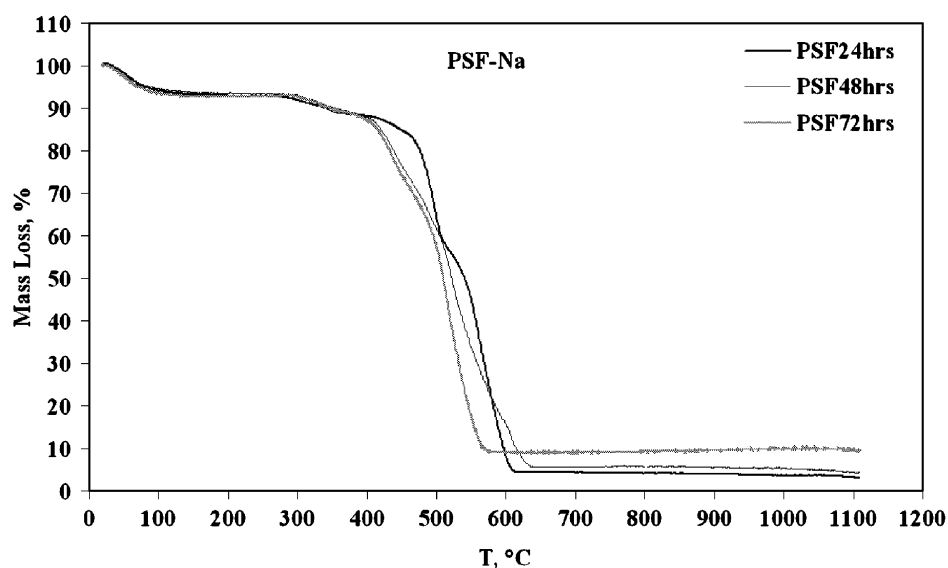


Fig. 3. TG analyses of sulphonated polysulphone powders in sodium form.

Table 1
Sulphonation degrees by thermal analysis

Sample	Sulphonic groups loss (%)	Residual mass at 900 °C (%)	Δ Mass loss (%)	SO ₃ H (%)
PSF-24 h (Na)	4.35	4.02	8.37	39
PSF-24 h (H)	7.33	–	7.33	43
PSF-48 h (Na)	4.38	5.53	9.91	47
PSF-48 h (H)	8.56	–	8.56	51
PSF-72 h (Na)	4.47	9.53	14.00	70
PSF-72 h (H)	11.23	–	11.23	69

percentage of mass loss are reported, considering the molecular mass of the sulphonic groups in the acid and sodium form. It is evident that the values were comparable.

The glass transition (T_g) temperature increases by increasing the degree of sulphonation, as is clear from Table 2.

Here, both the temperature at the point where the endotherm begins (onset temperature) and the T_g values for all samples are reported. The position of the glass transition shifts slightly upward with increase of the sulphonic groups as reported in Fig. 5.

The introduction of sulphonic groups in a ring of bis-phenol A unit supplies a more rigid structure. In fact, the sulphonic group causes intra and inter chain bridges due to strong hydrogen bonds between sulphonic groups or SO₂ groups of the polymer backbone. These intermolecular interactions limit the internal rotation of sulphonated

phenyl rings, which is in contrast to unsulphonated PSF. Moreover, the presence of DMAc residue in membranes produces a decrease of T_g value, probably due to the interaction between dimethylamine, SO₃H and SO₂ groups [18,19] that inhibits the intra–inter chain bridges. In fact, the T_g value for the PSF Aldrich membrane is lower than PSF Aldrich pellets.

The FT-IR spectra in the region 1050–1000 cm⁻¹, relative to untreated and sulphonated PSF with different degrees of sulphonation, are reported in Fig. 6.

In the frequency ranges 1050–1000 cm⁻¹ [20], two characteristic trends are highlighted. In particular, the band located at 1014 cm⁻¹ is assigned to the symmetric stretching vibration of the diphenyl ether unit, while the peak at 1028 cm⁻¹ is due to the symmetric stretching vibration of the sulphonated group. Considering that the peak at 1014 cm⁻¹ is invariant with the increase of degree of sulphonation, all the spectra have been normalised using this peak. It is evident that the symmetric peak at 1028 cm⁻¹ increases with increasing sulphonation level.

In Table 3, the physico-chemical characterisation results on the membranes are reported.

From the IEC value, the degree of sulphonation of the polymer was determined. These results are comparable to degree of sulphonation of polymer powders obtained from TG analyses.

An increase of IEC and water uptake with the reaction time was observed and the PSF-48% shows values comparable to the commercial

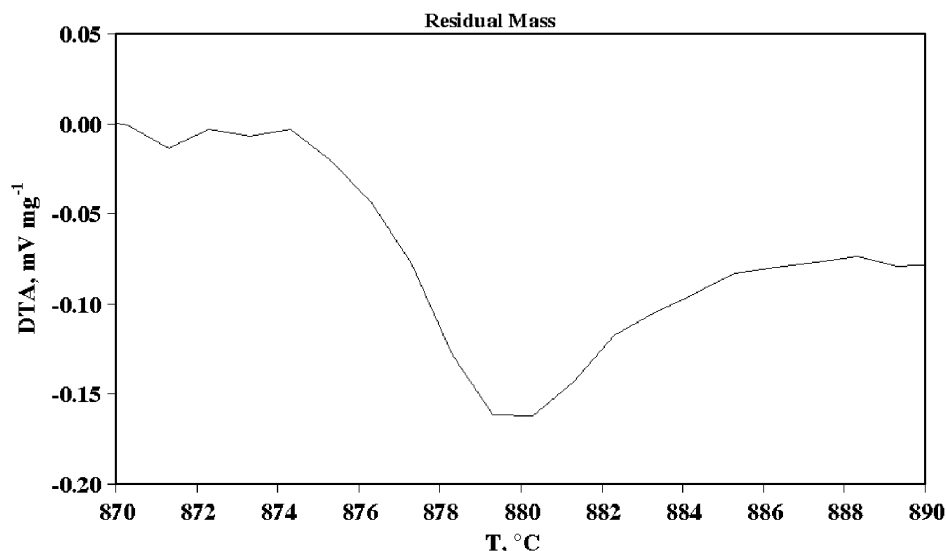


Fig. 4. Residual screening by DSC analysis.

Table 2
Glass transition temperatures in sulphonated polysulphone membranes

Sample	Onset (°C)	T_g (°C)
PSF Aldrich membrane	182.2	183.5
PSF Aldrich pellets	190.3	190
PSF-40%	204	206.8
PSF-48%	205.3	208.6
PSF-69%	205.5	209

N112 measured under the same experimental conditions.

The IEC and Wup% values for the commercial N112 supplied by DuPont [21] are different because they were measured under different experimental conditions.

The similarity between PSF-48% and N112 could be explained by taking into account the equivalent weight of the two different polymers. In fact, Nafion has a sulphonic group per each repeat unit ($EW = 1100 \text{ g mol}^{-1}$), while PSF with a degree of sulphonation of about 50% (PSF-48%) contains about one sulphonic group per two monomeric units ($EW = 1000 \text{ g mol}^{-1}$), meaning that the sulphonic group distribution is almost the same in the two polymers.

To simulate the operative cell conditions on these PSF membranes, the water uptake was determined at different temperatures (60, 80 and 100 °C).

As is highlighted from the results reported in Fig. 7, the water uptake slightly increases with the

increase of temperature for all the samples, except for the highly sulphonated sample (PSF-69%) which shows a significant swelling at 100 °C if compared to other samples.

Table 4 reports the methanol permeability of the sulphonated PSF membranes and commercial N115 membrane at room temperature.

The thickness of PSF membranes are similar to N112, so a comparison was effected by using N115 as a reference. The methanol permeability of N115 membrane is $1.04 \text{ exp}^{-06} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, which is similar to the literature result of $1.17 \text{ exp}^{-06} \text{ cm}^2 \text{ s}^{-1}$ [22]. The methanol permeability of sulphonated PSF membranes increases by increasing the degree of sulphonation. However, the PSF membrane with a higher degree of sulphonation shows a methanol permeability lower than the N115 membrane, respectively, $1.66 \text{ exp}^{-07} \text{ cm}^2 \text{ s}^{-1}$ against $1.04 \text{ exp}^{-06} \text{ cm}^2 \text{ s}^{-1}$; in other words the sulphonated PSF membranes have a lower methanol permeability (one to two orders of magnitude) compared to N115 membrane.

This aspect is more evident in Fig. 8, which reports the methanol permeability values as a function of the degree of sulphonation.

The sulphonated PSF membranes were tested in a single cell in the temperature range 80–120 °C with 100% RH.

In Fig. 9, the cell resistance for all tested membranes is reported and compared.

It is important to observe how the behaviour of the membranes with different degrees of sulphonation is different as a function of the cell temperature.

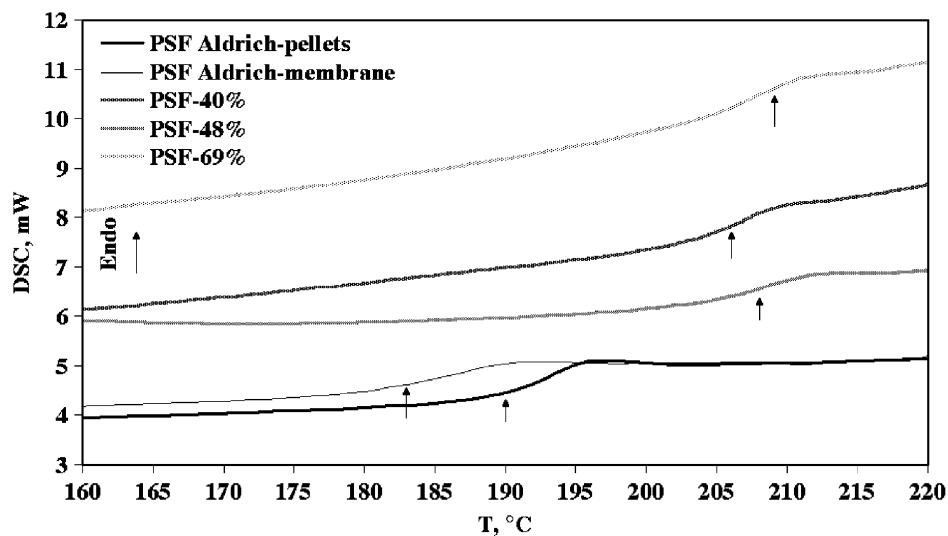


Fig. 5. Glass transition temperatures in sulphonated polysulphone membranes.

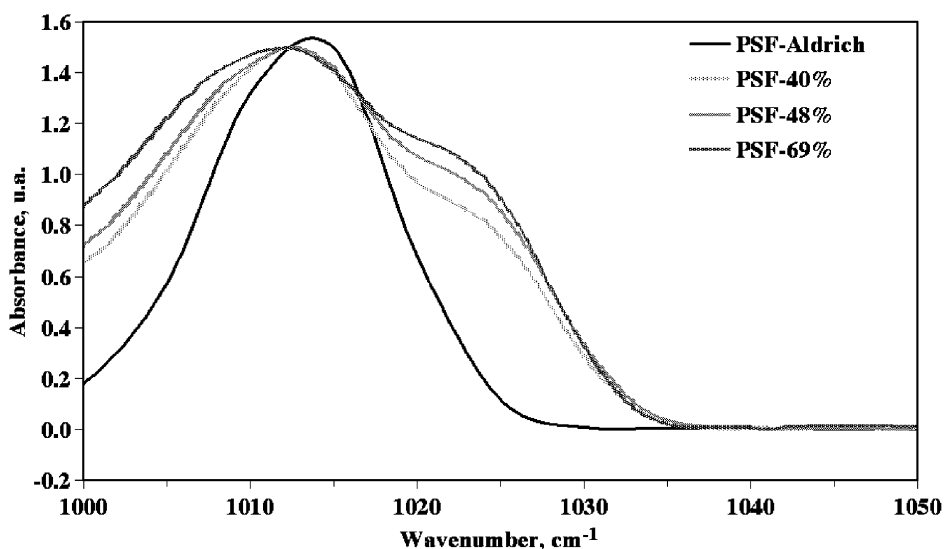


Fig. 6. FT-IR spectra of sulphonated PSF membranes in the region between 1000 and 1050 cm^{-1} .

Table 3
Physico-chemical data for polysulphone membranes

Sample	Sulphonation time (h)	IEC (meq g^{-1})	SO_3H (%)	EW^{b} (g mol^{-1})	Thickness (μm)	Wup at RT (%)
PSF-40%	24	0.85	40	1176	61	14
PSF-48%	48	1	48	1000	84	20
PSF-69%	72	1.39	69	719	61	26
N112 exp	–	0.93	–	1075	50	21
N112 ^a	–	0.89	–	1124	51	38

^aSupplied by DuPontTM; the water uptake value taken at 100 °C for 1 h.

^bCalculated by IEC values.

As expected, the membrane with the highest sulphonic groups content (PSF-69%) shows the lower cell resistance due to a high proton conductivity, but

a further increase of the temperature (over 100 °C) produces a dramatic increase of this value due to the swelling effect related to the a high sulphonation

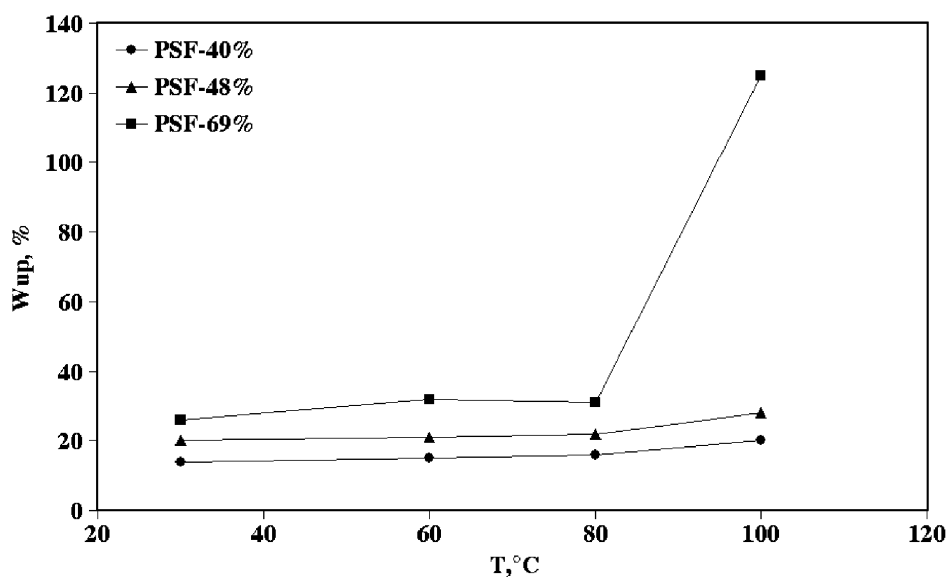


Fig. 7. Wup trend in function of T (°C).

Table 4
Methanol permeability values on sulphonated polysulphone membranes

Membranes	Methanol permeability ($\text{cm}^2 \text{s}^{-1}$)
Nafion 115 experimental	$1.04 \text{ exp}-06$
Nafion 115 literature	$1.17 \text{ exp}-06$
PSF-40%	$2.67 \text{ exp}-08$
PSF-48%	$5.93 \text{ exp}-08$
PSF-69%	$1.67 \text{ exp}-07$

level. The membrane with the lowest sulphonic group content (PSF-40%) shows the highest cell resistance at all temperatures, probably due to its low proton conductivity. The best behaviour was observed for the PSF-48% membrane. A sulphonic group content of about 50% is, probably, a good compromise between proton conductivity and cell resistance value.

In Table 5, the OCV and cell resistance values are reported for the tested membranes.

The measured OCV value for the PSF-48% membrane is higher than the commercial membrane (0.943 V for PSF against 0.862 V for N112). This difference cannot be attributable only to the difference of thickness, but indicates a lower gas permeability of PSF polymer.

The PSF-69% has good OCV and low cell resistance values in the range 80–100 °C (Figs. 10 and 11); by increasing the temperature to over 100 °C a decrease in the OCV and increase in cell resistance values occurs.

These results are in accordance with the physico-chemical data; in fact at temperatures up to 80 °C a restrained swelling is suitable for good proton conduction, while an irreversible swelling starts at 100 °C causing the OCV value drop.

The comparison at 120 °C (Fig. 12) highlights complete degradation of the PSF-69% membrane.

The PSF-48% shows a slight OCV and a pronounced cell resistance value decrease by increasing the temperature, maintaining a higher performance than the other two membranes over all the investigated range of temperature. This sample did not present irreversible swelling at 100 °C; in fact a performance improvement was observed at $T > 100$ °C. In this case, a power density of 360 mW cm^{-2} at 0.6 V was recorded.

The performance of PSF-40% could be explained through the high resistance and low OCV values up to 110 °C, while at 120 °C the good OCV and a low cell resistance values explain the improved performance. The swelling data are in accordance with these results, in fact the swelling only starts at 100 °C for this sample.

The membrane having about 48% SO_3H was chosen for the comparison with a commercial N112 membrane. The IR-free (for the different thickness) polarisation curves at 120 °C are shown in Fig. 13.

The performance loss at high current density for the PSF membrane could be associated with a non-optimised electrode structure for this polymer due

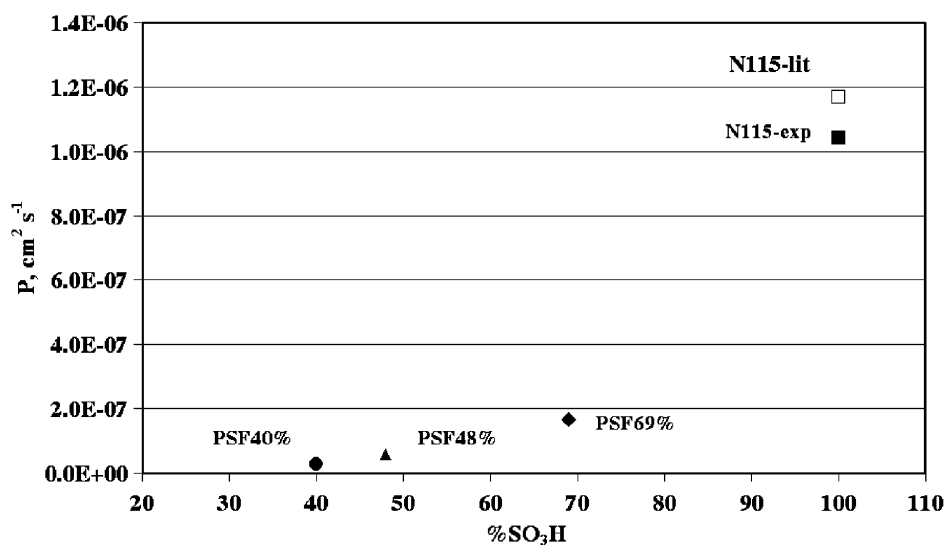


Fig. 8. Permeability trend on sulphonated PSF membranes related to the sulphonation degree.

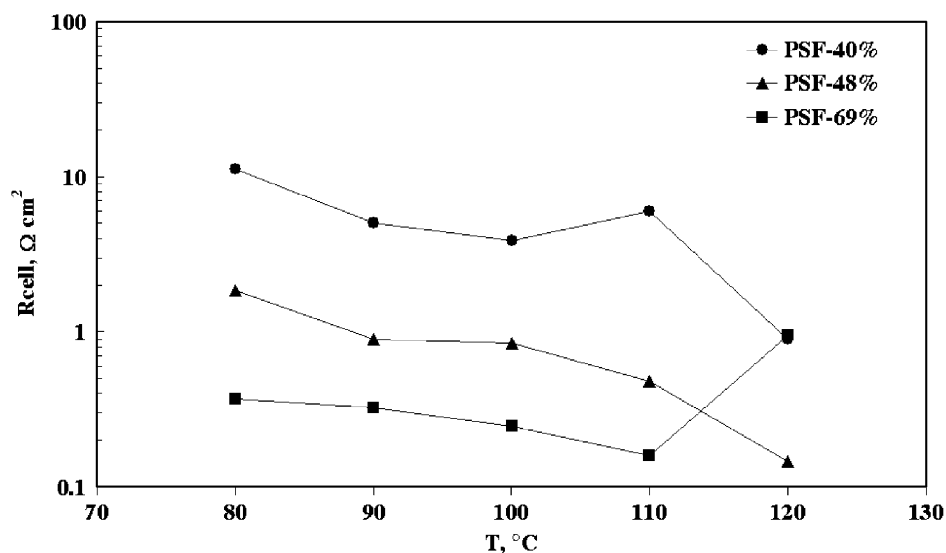


Fig. 9. Cell resistance trend as a function of T (°C).

Table 5

Electrochemical data for sulphonated membranes in the temperature range 80–120 °C

T_{cell} (°C)	PSF-40% (OCV, V)	PSF-48% (OCV, V)	PSF-69% (OCV, V)	PSF-40% (R_{cell} , Ω cm ²)	PSF-48% (R_{cell} , Ω cm ²)	PSF-69% (R_{cell} , Ω cm ²)
80	0.893	0.975	0.96	11.2	1.85	0.37
90	0.893	0.96	0.926	5	0.9	0.325
100	0.893	0.943	0.893	3.85	0.850	0.245
110	0.91	0.926	0.827	6	0.480	0.16
120	0.943	0.943	0.727	0.9	0.145	0.95

to the presence of a perfluorosulphonic ionomer in the catalyst layer of the electrodes. In conclusion, from physico-chemical and electrochemical data

obtained this type of polymeric membranes can represent a valid alternative to perfluorosulphonic membranes.

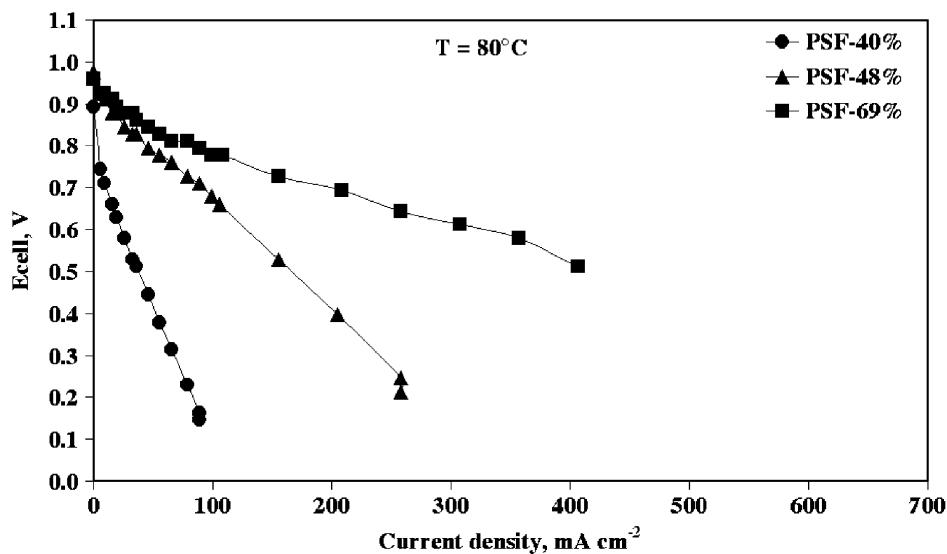


Fig. 10. Polarisation curves at 80 °C in humidified H₂/air for PSF with different sulphonation degree.

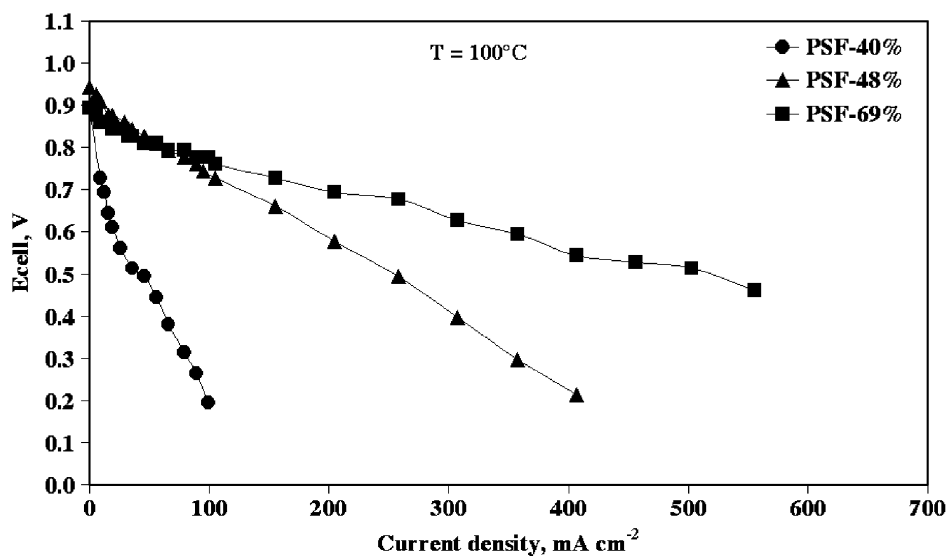


Fig. 11. Polarisation curves at 100 °C in humidified H₂/air for PSF with different sulphonation degree.

4. Conclusions

The sulphonated PSF synthesis was standardised by controlling the fundamental parameters that regulate the degree of sulphonation: temperature, time and molar ratio of the sulphonant agent.

Three different degrees of sulphonation for the polymer were used to prepare corresponding membranes that were characterised in order to obtain physico-chemical and electrochemical data.

DSC analyses highlighted that the T_g values for sulphonated PSF membranes slightly increased

with increase of the degree of sulphonation, from 206 to 209 °C.

The percent degree of sulphonation for the different films was observed by FT-IR investigation in the range 1000–1050 cm⁻¹, in particular, symmetric stretching vibrations of the sulphonated group on different sulphonated PSF membranes were observed at 1028 cm⁻¹.

The methanol permeability of sulphonated PSF membranes increased with increasing degree of sulphonation, and the PSF membrane with a higher degree of sulphonation showed a methanol permeability lower than the

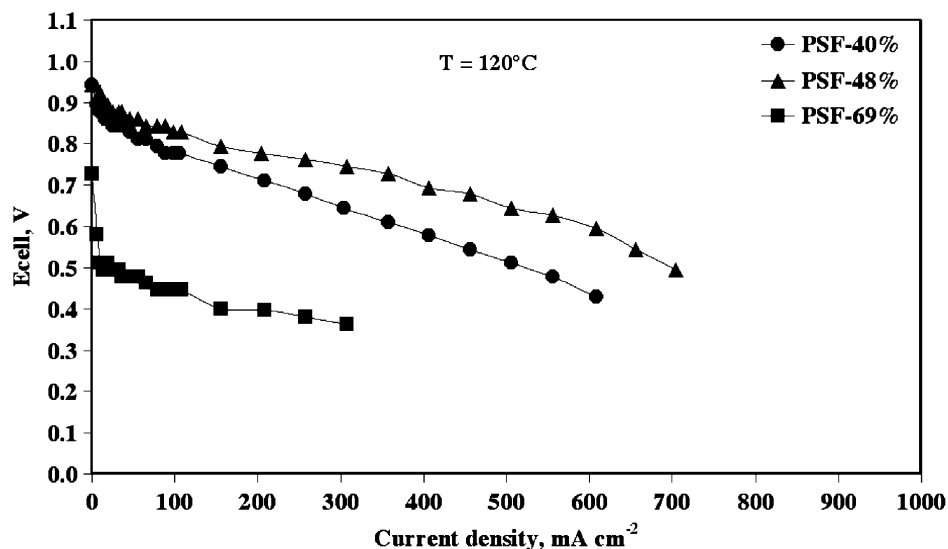


Fig. 12. Polarisation curves at 120 °C in humidified H₂/air for PSF with different sulphonation degree.

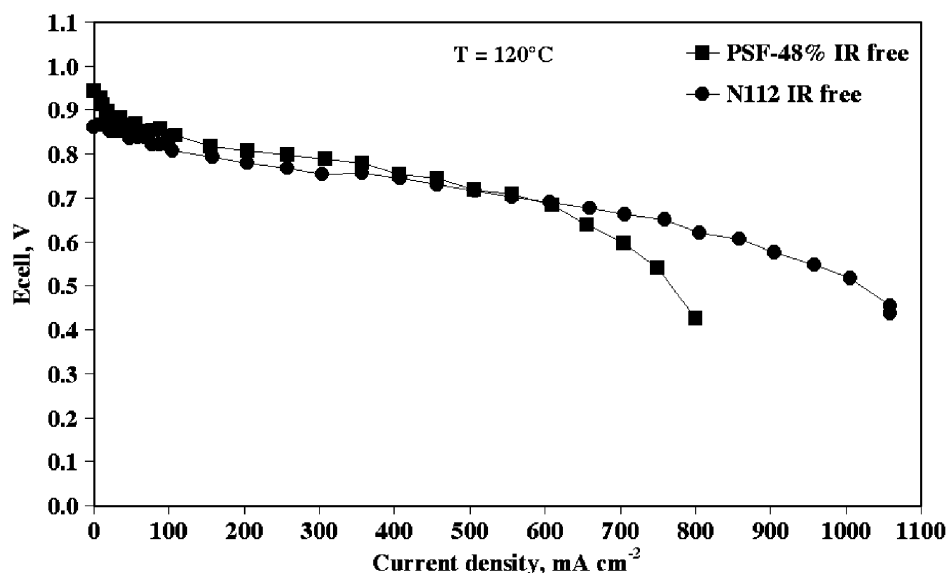


Fig. 13. Comparison between IR-free polarisation curves at $T = 120\text{ }^{\circ}\text{C}$ in humidified H₂/air for PSF-48% and N112.

N115 membrane, 1.67 and $1.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

The PSF-48% membrane was selected as the best compromise between physico-chemical and electrochemical characteristics. It was tested at $T = 120\text{ }^{\circ}\text{C}$ in humidified H₂/air, reaching a maximum power density of about 360 mW cm^{-2} at a constant cell potential of 0.6 V .

Moreover, the measured OCV value was found to be higher if compared to commercial Nafion, indicating a lower gas permeability related to the PSF polymer. These promising results make polymer a good candidate for further developments in research concerning a possible alternative to the perfluorosulphonic polymers.

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