

Sulfonated polysulfone ionomer membranes for fuel cells

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Received 25 September 2000; received in revised form 12 December 2000; accepted 17 January 2001

Abstract

Sulfonated polysulfone (SPSU) membranes with different sulfonation levels have been prepared and evaluated as proton exchange membranes in polymer electrolyte fuel cells (PEFC). The membranes have been characterized by ion-exchange capacity (IEC), thermal analysis, proton conductivity and single cell performance. The introduction of sulfonic groups in the base polymer produces an increase in glass transition temperature (T_g) from 190 to about 200–220°C and a thermal decomposition of polymer at lower temperature. Proton conductivity of $4.3 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 80°C on a SPSU membrane with IEC = 1.25 meq/g was obtained. Membrane/electrodes assemblies (MEAs) prepared with SPSU gave, in single cell tests at 80°C, power densities of 400 and 500 $\text{mW} \cdot \text{cm}^{-2}$ in H_2/air and H_2/O_2 , respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polysulfone; Sulfonated polysulfone; Proton conductivity; Fuel cell

1. Introduction

In recent years, great effort has gone into the development of polymer electrolyte fuel cells (PEFC) for both mobile and stationary applications [1–4].

A key issue in large-scale commercialization of PEFCs is the high cost of Nafion, the perfluorinated proton conductive material, commonly used as solid electrolyte in this application. As a consequence, a major research goal would be to identify and achieve novel, high performance, low cost proton conductive electrolytes. Many engineering thermoplastic polymers such as polysulfones, polyethersulfones, polyetherketones, polyimides, polybenzimidazole, polyoxadiazole, polyphosphazenes have been claimed

to be possible substitutes of perfluorinated ionomers, provided that a charge group (sulfonic) is introduced into the structural unit. Several ways to prepare partially perfluorinated and non-perfluorinated ionomer membranes are reported in literature, based on chemical modification of the polymers [5–8] or monomer sulfonation and subsequent polymerization [9,10].

Among the aforementioned polymers, the polysulfone (PSU) was considered more interesting for its low cost, commercial availability and processability and for this, we decided to investigate it in its form of sulfonated material. Previous papers reported two different procedures for the sulfonation of polysulfone. In a procedure, the sodium-sulfonated group was introduced in the base polysulfone via the metalation–sulfonation–oxidation process [11] and in others, the trimethylsilyl chlorosulfonate was used as the sulfonating agent [12].

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Recently, we have reported a mild sulfonation process to prepare proton-conducting membranes having a percentage of sulfonation from 23% to 53% [13]. The present paper reports the results related to samples of polysulfone membranes prepared with higher sulfonation levels, which should result in being more suitable for fuel cell application. The so-prepared sulfonated materials were evaluated in terms of ion-exchange capacity (IEC), thermal stability, proton conductivity and electrochemical performance in single cell configuration.

2. Experimental

The following procedure was used to prepare the sulfonated polysulfone (SPSU) samples. The polysulfone polymer Aldrich (Mn ca. 26 000, T_g 190°C) was dissolved in chloroform at 25°C, then treated with trimethylsilyl chlorosulfonate (Aldrich) to produce a silyl sulfonate polysulfone intermediate product. The amount of intermediate product depends on the mole ratio of sulfonating agent and polymer-repeated units. A slight excess of sodium methoxide was added to the solution to cleave silyl sulfonate intermediate and to obtain the final sulfonated product. All samples were vigorously washed with ethanol and rinsed several times with distillate water. For complete removal of the solvents, they were dried in an oven for 48 h at 110°C. The detailed preparation procedure is described elsewhere [13].

Membranes of sulfonated polysulfone were obtained by casting into a glass plate the polymer previously dissolved in dimethylacetamide (DMAc). The membranes were washed in distillate water and subsequently treated with 1 M HCl, for at least 15 h at 50–60°C, to obtain the acid form of the sulfonated polymer. Three different membranes (SPSU1, SPSU2 and SPSU3) with sulfonation degrees of 49%, 61% and 77% were prepared and tested.

A Carlo Erba CHNS-O analyzer model EA 1108 was used for elemental analysis of the membrane samples. Elemental analysis data were used to calculate the sulfonation degree and the theoretical ion-exchange capacity (IEC).

IEC was also determined via titration of the released amount of H^+ of the polymer in acid form in 1 M NaCl with 0.1 M NaOH by using phenolphthalein as indicator.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out (Netzsch model STA 409) in environmental air from room temperature to 950°C, with a heating rate of 5°C/min.

The proton conductivity was determined during fuel cell experiments by measuring the cell resistance by the current interruption method. This procedure consists of applying a trigger signal to the electronic load which switches-off the circuit when the cell is under galvanostatic operation at a suitable current density (200–400 mA · cm⁻²). The steep variation of cell potential, observed after current interruption, on the oscilloscope (Philips model 3375) is attributable to ohmic drop. Measurements were performed at the temperatures ranging from 25 to 90°C with the cell operating in H₂/O₂.

Fuel cell tests were carried out in a 5-cm² single cell (GlobeTech). Membrane/electrode assemblies (MEAs) were obtained by hot pressing the gas diffusion electrodes on the membranes. Electrodes with a low Pt content (0.1 mg cm⁻²) were home made by spraying technique using a mixture of the electrocatalyst (20% Pt/Vulcan XC-72 from E-TEK) with the Nafion solution (Aldrich, 5 wt.%) to increase the contact area. The electrochemical measurements in single cell were performed at 80°C in H₂/air and H₂/O₂ at 3.0 absolute bar with humidified gases. Further details on electrodes and MEA preparation as well as on fuel cell tests and related measurements can be found in a previous paper [14].

3. Results and discussion

The main characteristics of the SPSU membranes compared with Nafion 117 are reported in Table 1.

The SPSU1 and SPSU2 samples were evaluated by thermal analysis, proton conductivity measurements and fuel cell performance. The excessive swelling observed for the SPSU3 sample, when boiled in water, renders this material unsuitable for proton conductivity measurements and fuel cell tests at temperature above 80°C.

In Fig. 1, TG analysis results are reported for SPSU2 and SPSU3 membranes and compared with polysulfone (PSU) polymer. Although the analysis was performed from 25 to 950°C, only the region

Table 1
Characteristics of the SPSU and Nafion 117 membranes

Sample	Thickness (μm)	Sulfonation by elemental analysis (%)	IEC by elemental analysis (meq/g)	IEC by titration (meq/g)
Nafion 117	210		0.91	0.91
SPSU1	55	49	1.1	1.1
SPSU2	90	61	1.25	1.41
SPSU3	70	77	1.53	1.60

between 25 and 550°C is analyzed because, at higher temperatures, the decomposition of the sulfonated polymers occurs. Two weight losses for SPSU samples are evidenced. At these losses, two endothermic peaks correspond in DSC analysis of Fig. 2. The first, around 100°C is related to the desorption of water bonded to the sulfonic groups. This is confirmed by analyzing the TG spectrum of the sample SPSU3 pre-heated at 160°C for 24 h. This thermal treatment does not produce significant modifications in the material except for the disappearance of the first peak. The second narrow endothermic peak between 230 and 250°C, not present in the PSU starting material, is due to a desulfonation process [15,16] occurring before polymer decomposition. From DSC analysis, the glass transition temperature (T_g) of SPSU samples appears to occur in the range between 200 and 220°C; the precise determination of this value is hindered by the desulfonation process occurring in the close region of temperature. In any case, T_g for SPSU is higher than that of the base polysulfone (190°C). Moreover, sulfonate samples

show lower decomposition temperatures with respect to PSU. This difference could be explained by an enhanced asymmetry in the polysulfone structure due to the introduction of SO_3 groups that renders it less regular, and therefore, less stable.

Proton conductivity of the membranes was calculated from resistance measurements in the temperature range from 25 to 90°C. The conductivity data are analyzed in terms of Arrhenius plot, as reported in Fig. 3, where the SPSU samples are compared with Nafion 117 membrane. The activation energies (E_a) derived from the Arrhenius plots are reported in Table 2. A value of E_a of 9.7 kJ/mol is found for Nafion 117, in agreement with literature data [17–19]. The E_a values for SPSU samples are only slightly higher than that of Nafion 117, and no particular deviations are found in the investigated range of temperature. Therefore, no differences in the conduction mechanism are evidenced, thus envisaging similar ion morphology for perfluorinated and aromatic ionomer membranes. Nafion 117 (IEC = 0.91 meq/g) has higher conductivity and lower E_a with

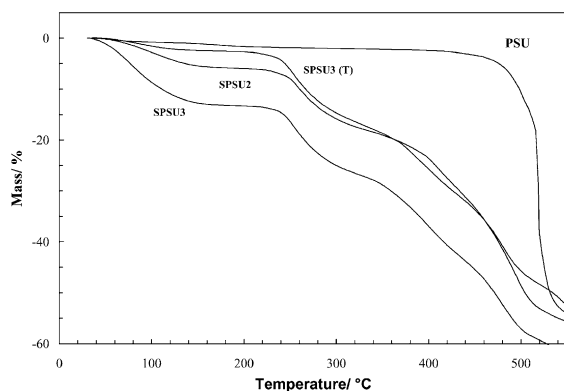


Fig. 1. TGA of PSU and SPSU membranes in the temperature range from 30 to 550°C in air.

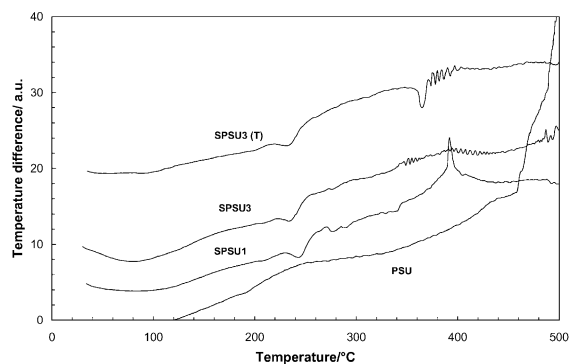


Fig. 2. DSC of PSU and SPSU membranes in the temperature range from 30 to 500°C in air.

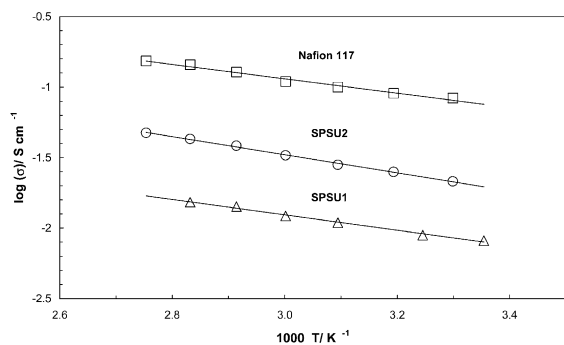


Fig. 3. Arrhenius plot of proton conductivity of SPSU and Nafion 117 membranes vs. temperature.

respect to the SPSU samples; this is attributable to the high hydrophobicity of C–F chains and large phase separation. In the SPSU samples, the conductivity increases with IEC, and values of 8.1×10^{-3} and $2.7 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, obtained at 25°C for the samples SPSU1 and SPSU2, respectively, are in agreement with that reported in Refs. [11,12] on membrane samples of comparable IEC. These values are similar to that measured for Nafion 117. The SPSU3 membrane is not completely stable in boiling water and because of, it has been less investigated.

The polarization curves in H_2/O_2 of MEAs prepared with SPSU1, SPSU2 and Nafion 117 membranes are reported in Fig. 4. As expected, SPSU1-MEA (with lower proton conductivity) shows poor fuel cell performance, whereas SPSU2-MEA exhibits a behavior very similar to that of Nafion 117 or even better if iR-free curves are considered. The low proton conductivity of SPSU2, which is 3.5 times lower than Nafion 117 membranes, is compensated

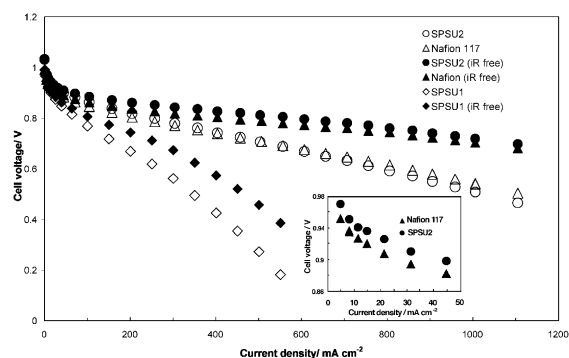


Fig. 4. Comparison between the polarization curves of MEA with Nafion 117 and SPSU membranes in H_2/O_2 at 80°C with 3/3 bar abs. of gas pressure: Black symbols are for iR-free curves.

by the lower thickness (90 vs. $210 \mu\text{m}$ of Nafion 117 as reported in Table 1), and thus, the measured cell resistances present only slight differences (0.21 and $0.16 \Omega \cdot \text{cm}^2$ for SPSU2 and Nafion 117, respectively) and almost the same fuel cell performances are obtained.

Moreover, lower cell voltages in the low current density region (0 – $50 \text{ mA} \cdot \text{cm}^{-2}$, see insert in Fig. 4) was measured for Nafion 117 with respect to SPSU2 membranes, denoting the occurrence of parasitic chemical reactions caused by the gas permeability through the membrane. Because the Nafion 117 membrane is 2.4 times thicker with respect to the SPSU2 membrane, it is evident that the latter material is less permeable to the reagent gases.

The cell voltage and power density as a function of the current density for SPSU2 sample are shown in Fig. 5. Power densities of about 400 and $500 \text{ mW} \cdot \text{cm}^{-2}$ were achieved at 80°C and 3 bars of pressure in H_2/air and H_2/O_2 operation, respectively. These results are very promising if we consider that they were obtained starting from such a versatile and inexpensive material and by using electrodes optimized for the Nafion–MEA and not for the SPSU–MEA.

Unlike that found for proton conductivity, the H_2/O_2 fuel cell performance recorded in this work is higher with respect to that reported in Refs. [11,12]. The lower performance reported in Ref. [11] with the membrane having IEC comparable with SPSU2 sample, is probably due to unsuitable electrodes or fuel

Table 2

Activation energy values (E_a) calculated on SPSU and Nafion 117 membranes

Sample	Temperature range ($^\circ\text{C}$)	E_a (kJ/mol)
Nafion 117	30–90	9.71
		7.82 [17]
		9.42 [18]
		13.43 [19]
SPSU1	25–80	10.38
SPSU2	30–90	12.26

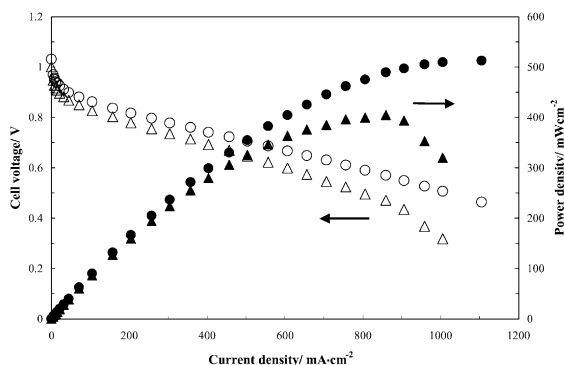


Fig. 5. Cell voltage (empty symbols) and power density (black symbols) vs. current density for MEA with SPSU2 membrane in H_2/O_2 (O) and H_2/air (Δ) operation. Fuel cell test conditions: $T = 80^\circ\text{C}$; $P(\text{H}_2/\text{O}_2 \text{ or air}) = 3/3$ bar abs.

cell hardware. With respect to Ref. [12], a lower performance was obtained with a membrane of $\text{IEC} = 1.07$ meq/g filled with an inorganic solid proton conductor.

4. Conclusions

A mild sulfonation process was successfully used to produce ion-exchange membranes with polysulfone as a polymer for PEFCs. Membranes of sulfonated polysulfone with an IEC ranging from 1.1 to 1.5 meq/g were easily prepared by a phase inversion technique and evaluated. Thermal analysis measurements show an increase in glass transition temperature (T_g) for the sulfonated membranes with respect to the base polysulfone, although this could not be determined precisely for a probable desulfonation process occurring in the close temperature range. The decomposition temperature of the main chain decreases by increasing the sulfonation degree. An increase of the sulfonic groups produces an asymmetry in the polysulfone structure, making it less stable.

The proton conductivity of SPSU membranes is lower than Nafion 117 membrane. Arrhenius plots of the proton conductivity were obtained without deviation in the investigated range of temperature from 25

to 90°C , suggesting a similar conduction mechanism for the aromatic and perfluorinated ionomer membranes.

Power densities of 400 and $500 \text{ mW} \cdot \text{cm}^{-2}$ in H_2/air and H_2/O_2 , respectively, were obtained during the fuel cell tests with unoptimized electrodes.

Moreover, in spite of the lower thickness of investigated SPSU2 membranes with respect to Nafion 117, it has been shown, in the fuel cell test, higher voltages in the region of low current densities (from 0 to $50 \text{ mA} \cdot \text{cm}^{-2}$), indicating a lower permeability of reagent gases through the membranes.

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