

New Sulfonated Polysulfone Co-Polymer Membrane for Low Temperature Fuel Cells

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(Received June 26, 2003; received revised form September 23, 2003)

Abstract: Membranes based on a new sulfonated polysulfone co-polymer having a pending lactone cardo group in one of the structural units were characterized by ion-exchange capacity, water-up take, thermogravimetric analysis and differential scanning calorimetry. This sulfonated polysulfone co-polymer is characterized by a low glass transition temperature (138°C). Single cell tests in H₂/air fuel cells configuration at 30 and 60°C have shown for 120 μm membranes power densities of 140 and 210 mWcm⁻² respectively. A stable time performance was measured up to 250 hours.

Key words: sulfonated polysulfone co-polymer, membrane electrode assembly, fuel cell.

1. INTRODUCTION

At present, perfluorinated polymers based on perfluorosulfonic acid, such as Nafion® (Du Pont), are the most commonly used materials as proton-conducting electrolyte membranes in low temperature fuel cells. 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. Many studies have been carried out to provide cheaper alternatives to these membranes.

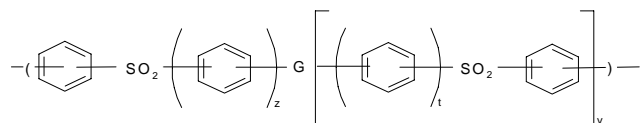
Aromatic polymers such as polysulfones, polyethersulfones, polyetherketones, polyimides, polybenzimidazoles [1-3], were proposed as substitutes of perfluorinated materials, provided that an acidic functional group (e.g., sulfonic acid group, carboxylic acid group and phosphoric acid group) is

introduced into the structural unit. These materials met most of the specifications of the fuel cell membranes, namely high protonic conductivity, stability in oxidant and reducing environments and acidic medium, thermal stability, etc. Among the above-mentioned polymers, polysulfone is considered as very interesting due to its low cost and commercial availability [2, 4-7].

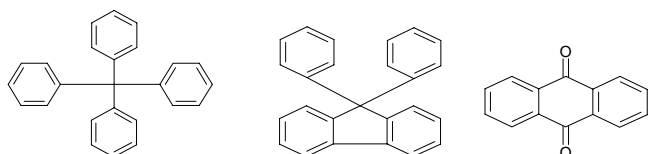
The synthetic routes to the synthesis of sulfonated polysulfones are based on the use of commercially available polymers, such as Udel® (Solvay) or its alternatives, usually prepared in industry by Williamson condensation of dichlorodiphenylsulfone with disodium salt of Bisphenol A, followed by sulfonation with known sulfonating agents such as chlorosulfonic acid, acetylsulfate, trimethylchlorosulfonic acid, etc. [8-10]. However, recently have appeared some works [11, 12], devoted to the application of so-called cardo polysulfones or polyethersulfones for preparation of ion conducting membranes for polymer electrolyte membrane fuel

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cells. These polymers include at least one of the following moieties:

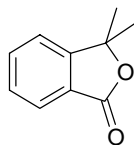


where G is:



These, polymers usually possess lower glass transition temperature (T_g) in respect to the traditional sulfonated polysulfones and elevated solubility in organic solvents. Both these factors make easier their processability and membrane electrode assembly (MEA) fabrication. More particularly, a low T_g reduces the temperature required for assembling the electrodes with the membrane, and a possible degradation of the sulfonic groups is avoided.

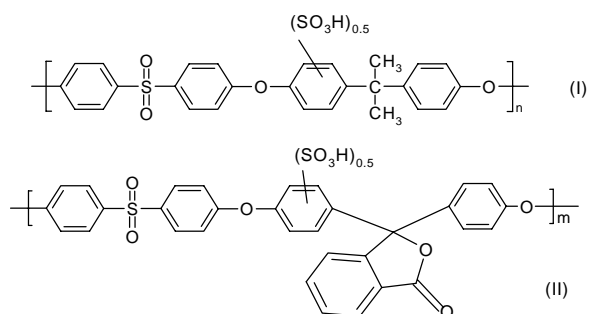
This work presents the results regarding the characterization of membranes based on a sulfonated polysulfone co-polymer having the following a pending lactone cardo group in one of its monomeric unit:



The membranes were characterised both thermally (differential scanning calorimetry and thermogravimetric analysis) and physicochemically (water up-take and ion exchange capacity), and it was evaluated its performance in H_2 /air fuel cell configuration at low temperature (30-60°C). The performance of 120 μm membranes assembled with commercial electrodes (E-TEK, Inc.) is comparable to Nafion 117 assembled with the same electrodes, although it is evident that the performance of the polysulfone co-polymer based MEA is limited by a higher cell resistance.

2. EXPERIMENTAL

The sulfonated polysulfone co-polymer (SPS) membranes with the following chemical structure



where $n = m$, were received from Joint Stock Company "NPO Chemplast" (Russia).

The co-polymer was prepared by traditional synthetic route based on condensation of dichlorodiphenylsulfone with disodium salt of Bisphenol A and phenolphthaleine (mol ratio 2:1:1), followed by sulfonation with chlorosulfonic acid. The degree of sulfonation of the tested co-polymer corresponds to approximately one sulfonic group for two structural units. The structure of the sulfonated co-polymer was confirmed by both NMR and IR.

The films were prepared by solution casting from 10-15% sulfonated polysulfone co-polymer solutions in DMA/TCE, having an average thickness of 123 μm (checked with Mitutoyo Corp. Model ID-C112PB thickness gauge on the bare sample).

For thermal characterization the samples were used as received, while for physicochemical characterization and fuel cell tests the membranes were first activated in 30% aqueous H_2SO_4 solution at room temperature for 18 hours and then washed with hot distilled water (50-60°C).

Thermogravimetric analysis (TGA) was carried out using a Metler Toledo Star System under N_2 flow with an heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$. The glass transition temperature (T_g) was measured using a Metler Toledo Star System differential scanning calorimeter (DSC) always under N_2 flow. Two scans were conducted at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from -20°C to 240°C . The T_g value was reported as the change in the midpoint in the slope of the baseline of the second scan.

The swelling characteristics were determined by water uptake measurements (WU). The membranes were dried in a vacuum oven at 80°C and weighted (m_{dry}), and than were immersed in distilled water for 24 hours at room temperature and its weight (m_{wet}) determined after eliminating the excess of water with filter paper. The water uptake value is obtained using the following equation:

$$\text{WU}\% = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (1)$$

The Ionic Exchange Capacity (IEC) expressed as moles of sulfonated repeated polymer monomeric unit for 1 gram of dry polymer, was determined through acid-base titration using an automatic titrator (Metrhom Mod.751GPD Titrimo). After weight determination of the membranes in the dry form (m_{dry}), they were immersed in $1 \text{ mol}\cdot\text{dm}^{-3}$ NaCl for 18 hours at 60°C in order to exchange H^+ ions from the polymer with Na^+ ions present in the solution. The solution containing the membrane was titrated with a $0.01 \text{ mol}\cdot\text{dm}^{-3}$ NaOH, monitoring pH during the titration. Plotting the pH as function of the NaOH added volume, the equivalent volume (V_{eq}) was determined and the IEC calculated according to the equation:

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

The electrochemical characterization was done under H_2 /air fuel cell configuration at 30 and 60°C, using humidified gases (100% relative humidity) at 1 bar abs. Hydrogen and air were fluxed respectively at 1.5 and 2 times the stoichiometry fixed for 1 A.cm⁻². A 5 cm² single cell test apparatus purchased from Globe Tech Inc. was used, and the membrane electrode assemblies were prepared by cold pressing the gas diffusion electrodes on the membrane surface. E-TEK Inc. commercial electrodes with 0.6 mg.cm⁻² Pt loading activated with a Nafion solution (Aldrich, 5 wt.%) were used.

After inserting the MEA into the single cell test housing, the cell was equilibrated with the humidified gases. Cell resistance was measured at the fixed frequency of 1 kHz and under open circuit by the impedance bridge (HP). The polarization curves were recorded with a program using an electronic load interfaced with a personal computer.

Short term stability tests were performed at constant potential at 30°C with start up in the morning and shut down after about 5 hrs each day, while at 60 °C in continuous mode.

The performance of both SPS and Nafion 117 (Du Pont) membranes were compared either in terms of physical chemical parameters and fuel cell performance. The same membrane electrode assembly configuration was used.

Before use, the Nafion 117 membrane was purified in 5% H_2O_2 solution at 80°C for 1 hour followed by a second treatment in 1mol.dm⁻³ H_2SO_4 for 2 hours. The Nafion based MEA was then prepared by hot pressing the electrodes and the membrane at 130°C for 3 min applying a 20 Kg cm⁻² pressure.

3. RESULTS AND DISCUSSION

3.1. Thermal characterisation (TGA and DSC)

Figures 1 and 2 report respectively the TGA and DSC thermograms of the studied sulfonated polysulfone co-polymer. The TGA curve reports the membrane dehydration process around 100°C, followed by degradation of the sulfonic groups at 220° C. The DSC analysis shows the glass transition at 138°C, and besides this process no other phase transients are observed in the scanned temperature range. The measured glass transition temperature is significantly lower than the onset temperature for the decomposition of the sulfonic groups.

The lower the glass transition temperature is, lower is the temperature required for assembling the electrodes with the membrane. In this way it is avoid a possible degradation of the sulfonic groups, the most sensitive part of the polymer structure.

Low Tg values also correspond to higher solubility in solvents, which entails a higher workability of the polymeric materials.

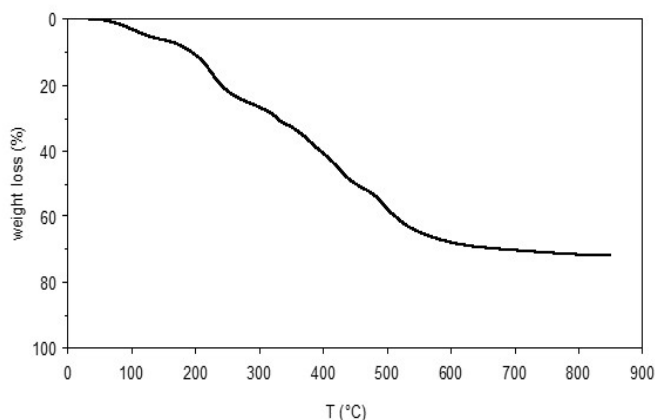


Figure 1. Thermogravimetric profile of the sulfonated polysulfone co-polymer membrane.

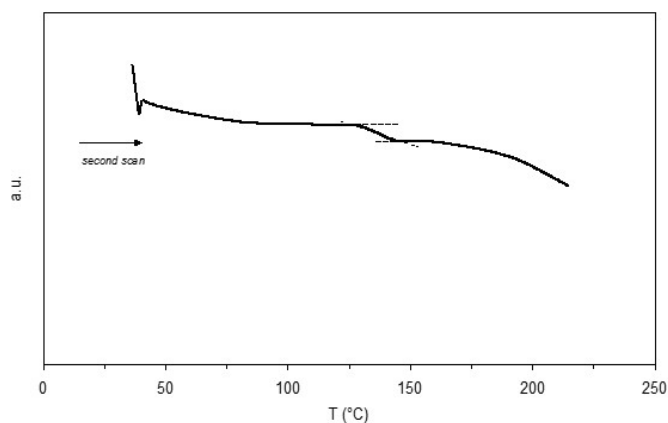


Figure 2. Differential scanning calorimetry thermogram of the sulfonated polysulfone co-polymer membrane.

3.2. Physicochemical characterization (WU and IEC)

Table 1 presents the experimental IEC and WU values of the sulfonated polysulfone co-polymer membrane, and the corresponding values of the Nafion 117 membrane were also included for comparison. The measured ion exchange capacity values was 1.13 meq.g⁻¹, which is in good agreement with the expected one calculated from the structural formula presented above (0.96 meq.g⁻¹). The ion exchange and hydration capacities of this co-polymer membrane are slightly higher than those of Nafion 117 membrane.

3.3. Fuel cell performance (H_2 /air configuration)

Figure 3 presents the polarisation curves recorded at 30 and 60 °C in air using the 120 μm thick sulfonated polysulfone

Table 1. Thickness, water up-take (WU) and ion exchange capacity (IEC) of the sulfonated polysulfone co-polymer (SPS) and Nafion 117 membranes.

Membrane	Thickness (μm)	WU (%)	IEC (meq.g^{-1})
SPS	123	44	1.13
Nafion 117	180	27	0.9

membrane. The open circuit voltage and cell resistance values measured at both temperatures are reported in Table 2.

The measured open circuit voltage values at both temperatures were very high indicating a reduced permeability of the gases through the membrane. High cell resistance values were also measured at both temperatures, and this limits the performance of these MEAs under polarisation. However, relatively high power densities of 130 and 225 mW.cm^{-2} were obtained at 30 and 60°C, respectively.

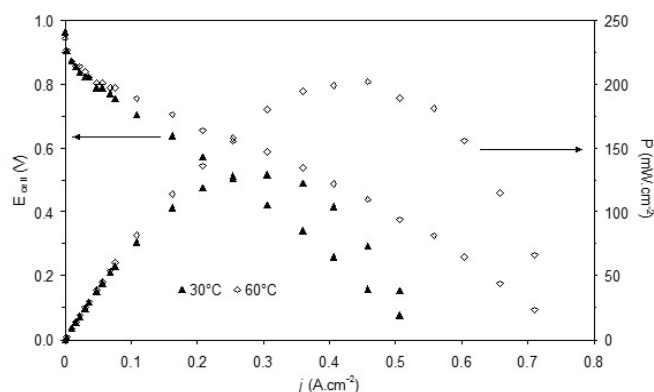


Figure 3. Polarisation curves of 123 μm sulfonated polysulfone co-polymer membrane in H_2/air fuel cell configuration at 30 and 60°C; membrane assembled with E-TEK, Inc. commercial electrodes with 0.6 mg.cm^{-2} Pt loading; Hydrogen and air (100% relative humidity) were fluxed respectively at 1.5 and 2 times stoichiometry fixed for 1 A.cm^{-2} .

Table 2. Cell resistance and open circuit voltage values measured at 30 and 60°C with sulfonated polysulfone co-polymer (SPS) and Nafion 117 membranes based MEAs.

Membrane	Thickness (μm)	30 °C		60°C	
		Rcell ($\Omega.\text{cm}^2$)	OCV (V)	Rcell ($\Omega.\text{cm}^2$)	OCV (V)
SPS	123	0.49	0.963	0.36	0.943
Nafion 117	180	0.25	0.976	0.20	-

Table 2 also presents for comparison the open circuit voltage and cell resistance values measured for the Nafion 117 based MEA at 30°C and 60°C. In Figure 4 the polarisation curves recorded for both MEA at 30°C are compared directly.

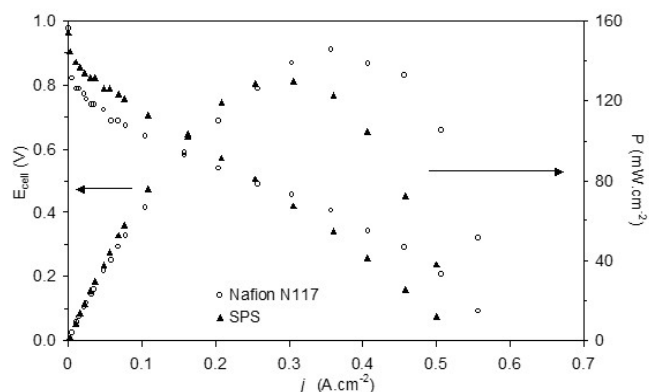


Figure 4. Polarisation curves of 123 μm sulfonated polysulfone co-polymer and Nafion 117 membranes in H_2/air fuel cell configuration at 30°C; membranes assembled with E-TEK, Inc. commercial electrodes with 0.6 mg.cm^{-2} Pt loading; Hydrogen and air (100% relative humidity) were fluxed respectively at 1.5 and 2 times stoichiometry fixed for 1 A.cm^{-2} .

Open circuit voltage values of the same order were obtained for both systems, with 123 μm sulfonated polysulfone co-polymer and 180 μm Nafion 117 membranes. Moreover, for current densities up to 200 mA cm^{-2} higher cell voltages were measured with SPS based MEA with respect to Nafion 117 based one. This different behaviour between the two materials was already observed by Lufrano et al. [13], and it was attributed to lower permeability to the reagent gases of the sulfonated polysulfone membranes.

Also the power output densities of both systems are of the same order, and it is clear that the higher cell resistance measured for sulfonated polysulfone co-polymer based MEA limits its performance.

These results are very encouraging since further improvements can be achieved by optimising the assembling procedure (e.g., hot pressing vs. cold pressing) and/or using specifically developed electrodes instead of standard commercial E-TEK ones.

Short term stability tests of the sulfonated polysulfone co-polymer membrane were performed at both 30 and 60°C, and the results are presented in Figure 5. Initially the cell voltage was kept at 0.2 V, and then gradually risen up to 0.4 V. The current drawn out of the cell under this voltage was followed in time for a total of 270 at 30°C and 160 hours at 60°C. No cells failure was recorded after this time but the tests were voluntarily interrupted. The recorded power densities are comparable to those obtained with the polarisation curves, and as shown in this figure the performance of these MEA's has good time stability.

4. CONCLUSIONS

It was shown that sulfonated polysulfone co-polymers have good electrochemical performance under low temperature H_2/air fuel cell conditions. The measured open circuit voltage

and power densities are comparable to those obtained with common commercially available Nafion 117 (Du Pont) membranes. The performance of the sulfonated polysulfone co-polymer based system is maintained in time.

Optimisation of the membrane electrode assembly (assembling procedure and structure) could probably lead to

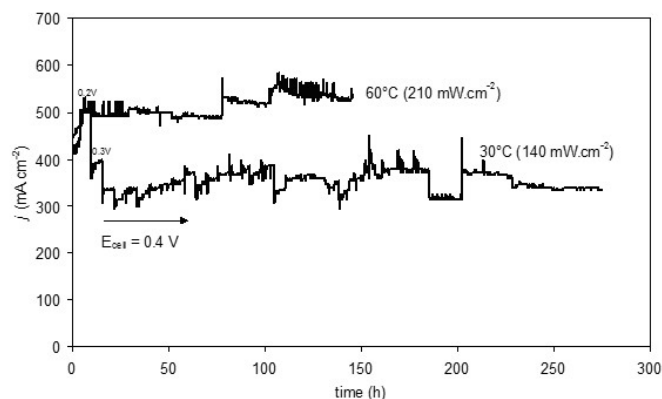


Figure 5. Constant potential time response of 123 μm sulfonated polysulfone co-polymer based MEAs in H_2/air fuel cell configuration at 30 and 60°C; membranes assembled with E-TEK, Inc. commercial electrodes with 0.6 $\text{mg}\cdot\text{cm}^{-2}$ Pt loading; Hydrogen and air (100% relative humidity) were fluxed respectively at 1.5 and 2 times stoichiometry fixed for 1 $\text{A}\cdot\text{cm}^{-2}$.

further improvements of the sulfonated polysulfone co-polymer based system.

Taken into consideration that polysulfones are low cost polymers widely available, commercialisation of its sulfonated form could represent a significant step towards the total cost reduction of the polymer electrolyte fuel cell system.

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