

Sulfonated Polysulfone as Promising Membranes for Polymer Electrolyte Fuel Cells

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ABSTRACT: A new, milder sulfonation process was used to produce ion-exchange polymers from a commercial polysulfone (PSU). Membranes obtained from the sulfonated polysulfone are potential substitutes for perfluorosulfonic acid membranes used now in polymer electrolyte fuel cells. Sulfonation levels from 20 to 50% were easily achieved by varying the content of the sulfonating agent and the reaction time. Ion-exchange capacities from 0.5 to 1.2 mmol SO₃H/g polymer were found via elemental analysis and titration. Proton conductivities between 10⁻⁶ and 10⁻² S cm⁻¹ were measured at room temperature. An increase in intrinsic viscosity with increasing sulfonation degree confirms that the sulfonation process helps to preserve the polymer chain from degradation. Thermal analysis of the sulfonated polysulfone (SPSU) samples reveals higher glass transition temperatures and lower decomposition temperatures with respect to the unsulfonated sample (PSU). Amorphous structures for both PSU and SPSU membranes were detected by X-ray diffraction analysis and differential scanning calorimetry. Preliminary tests in fuel cells have shown encouraging results in terms of cell performance. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1250–1257, 2000

Key words: sulfonation; sulfonated polysulfone; ion-exchange capacity; proton conductivity; fuel cell

INTRODUCTION

Ion-exchange membranes are used in several electrochemical processes such as in chloro-alkali production, water electrolysis, electro dialysis, and polymer electrolyte fuel cells.^{1,2} In these applications, the membrane must have a high chemical and electrochemical stability plus thermal and mechanical resistance at the operating conditions. In particular, for water electrolysis and in fuel cell applications, very low gases permeabilities are needed to avoid chemical reaction between oxygen and hydrogen. In addition, low ionic resistance is required to support high current density.

Until recently, only perfluorinated ionomer membranes could be successfully used for long times in these applications (up to 60,000 h of operation at 80°C).² However, they have some disadvantages such as high cost (\$600–1000/m²) and limited choices for thickness and ion-exchange capacity. Consequently, there is an increasing interest in the development of alternative ionomer membranes with lower cost, and higher proton conductivity, and that are more easily processed. In this respect, potential polymers for such uses include polysulfones, polyethersulfones, polyetherketones, polyimides, polybenzimidazoles, polyoxadiazole, and polyphosphazenes.

In several studies,^{3–8} the chemical modification of these polymers by different sulfonation processes have been reported. In some, direct

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polymer sulfonation was carried out in heterogeneous media using sulfuric or chlorosulfonic acid as both solvent and sulfonating agent.^{5–8} Sometimes this process shows phase separation between reagents and products during synthesis, and the formation of water-soluble polymers with low sulfonation degrees was disclosed.^{7,8} To overcome these problems, the sulfonation process was carried out in homogeneous media using chlorosulfonic acid (HSO_3Cl) on a polymer dissolved in a chlorinated solvent at temperatures between 0 and -10°C .^{9,10} However, the use of such a strong sulfonating agent as chlorosulfonic acid produces side reactions including crosslinking and cleavage of the polymer chains.^{7,8}

A different homogeneous sulfonation process was favourably carried out with a SO_3 -triethyl phosphate complex in dichloroethane solution, which was claimed^{11–13} to be more reliable and to minimize side reactions. However, the reaction with triethyl phosphate is very exothermic, plus the high reactivity and toxicity of SO_3 make it difficult to use.

Recently, Kerres et al.¹⁴ reported an alternative sulfonation process of commercial polysulfone based on a series of steps including metalation-sulfination-oxidation reactions. They improved the properties of the sulfonated material by using the sulfinate/sulfonate-containing products obtained in the previous steps to crosslink polymer chains^{15,16} through interchain sulfone formation.

An alternative method for sulfonation of small organic molecules is based on trimethylsilyl chlorosulfonate.^{17–19} It was recently used to produce a sulfonated polysulfone matrix filled with a solid protonic conductor.²⁰

In any case, it is evident that materials with different characteristics can be obtained depending on sulfonating agents, the base polymer, and the process used.

In this work, we report the results on the synthesis and characterization of sulfonated polysulfone polymer (SPSU) obtained using the trimethylsilyl chlorosulfonate as sulfonating agent at room temperature, together with some preliminary electrochemical tests of SPSU membranes in fuel cell application.

EXPERIMENTAL

Synthesis of SPSU and Membrane Preparation

The commercial polysulfone Udel (Amoco) was dissolved in chloroform at room temperature and

subsequently treated with trimethylsilyl chlorosulfonate (Aldrich) to produce a silyl sulfonate polysulfone. The amount of intermediate product formed was controlled by varying the mole ratio (0.7–1.4) between sulfonating agent and polymer repeat units and the reaction time of 24 and 48 h at room temperature. Sodium methoxide (Aldrich) was then used to cleave the silyl sulfonate moieties over 1 h to yield the sulfonated polysulfone. The sulfonated polymer solution was added dropwise to a nonsolvent bath of ethanol to obtain the precipitated product. The fine white polymer was then separated by filtration, vigorously washed with ethanol, and rinsed several times with distilled water. Finally, the sulfonated polysulfone polymer was dried in an oven for at least 48 h at 110°C for complete removal of solvents.

Transparent membranes of sulfonated polysulfone were obtained by dissolving about 1 g of polymer in 5–10 mL of *N,N*-dimethylacetamide (DMAc) and casting the polymer solution on a glass plate. Dry membranes with thicknesses ranging from 20 to 100 μm were obtained by varying the solvent amount or the distance between the gardner knife and the plate during the casting process. Finally, the membranes were converted into the acid form with 1M HCl (15 h at 50 – 60°C).

Physicochemical Characterization of PSU and SPSU 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. Before elemental analysis, all samples were vigorously washed many times with distilled water for complete removal of free acid, and then dried at 110°C for 48 h. After every three or four analyses, the instrument was then recalibrated with a sulfanilamide ($\text{C}_6\text{H}_6\text{N}_2\text{O}_2\text{S}$) standard sample (Carlo-Erba).

The ion-exchange capacity (IEC) was determined from both elemental analysis and via titration. A known amount of dry polymer (0.4–1.0 g) in acid form (after exchange in 1M of HCl at 80°C for 6 h) was suspended in 100 mL of a 1M NaCl solution under continuous stirring for not less than 18 h at 50 – 60°C . The released amount of H^+ was then determined by titration with a 0.1M NaOH solution using phenolphthalein as indicator. Nafion 117 membrane was used as reference material.

Dilute solution viscosity measurements were carried out using an Ubbelohde viscometer 0C in

a water bath thermostated at $25 \pm 0.05^\circ\text{C}$. Samples of PSU and SPSU were dried at 70°C under vacuum for 18 h, dissolved in DMAc at about 50°C under stirring, and filtered through a 0.2 mm paper filter (Whatman) before transfer into the viscometer. The efflux time for the solution was always above 200 s and each measurement was repeated at least five times. The specific (η_{sp}) and reduced (η_{red}) viscosities of the polymer solutions were measured at fixed concentration ($c = 0.2 \text{ g dL}^{-1}$) in DMAc.

From (η_{sp}) and (η_{red}), the intrinsic viscosities (η_{int}) were obtained using the Solomon–Ciuta²¹ equation:

$$\eta_{\text{int}} = [2 \cdot (\eta_{\text{sp}} - \ln \eta_{\text{red}})]^{1/2}/c$$

The thermal stabilities of the membranes were determined by thermogravimetry (TGA) and differential scanning calorimetry (DSC). The measurements were carried out with a Netzsch model STA 409 thermal analyzer in air from room temperature to 950°C and with a heating rate of $5^\circ\text{C}/\text{min}$.

The X-ray diffraction patterns of the PSU and SPSU films were obtained with a Philips model PW3710 X-ray diffractometer using a Cu-K α radiation source with a wavelength of 1.54 Å.

The swelling characteristics were determined by water uptake measurements. The samples were dried under vacuum for 18 h at 30 or 70°C and then weighed in sealed glass weighing bottles. They were then placed in distilled water at different temperatures between 25 and 100°C . Before subsequent sample weighing, the excess water on the membrane surface was removed with adsorbent paper. The water uptake was calculated from the weight difference between wet and dry membrane and reported as number of water molecules associated with each SO_3H group ($n \cdot \text{H}_2\text{O}/\text{SO}_3\text{H}$).

The proton conductivity was obtained by measuring the membrane resistance with a Universal Bridge LCR meter at 1 kHz. The tests were performed using a 50 cm^2 single cell over a range of temperatures between 25 and 80°C . Membranes were assembled with fuel cell standard electrodes fed with humidified nitrogen.

Electrochemical Characterization

Fuel cell tests on SPSU and Nafion 117 membranes were carried out at 80°C in a 50 cm^2 single cell. The electrodes were made by a spray tech-

nique following the procedure described elsewhere.²² A Nafion solution was added to the catalyst layer. This kind of electrode was used to produce membrane and electrodes assemblies (MEAs) with all the different membranes. The MEAs were obtained by hot pressing at 90°C and $200 \text{ kg}/\text{cm}^2$ of pressure.

RESULTS AND DISCUSSION

Sulfonation of PSU and Characterization of SPSU Membranes

Six different samples of SPSU were prepared by varying the content of sulfonating agent and reaction time. The sample characteristics (SPSU2 and SPSU3 differ only in reaction temperature) are reported in Table I.

From the S/C ratio obtained by elemental analysis, PSU appears to be easily sulfonated, with a sulfonation degree ranging from 20 to 50% at room temperature. The sulfonated samples (SPSU1) obtained with a lower amount of sulfonating agent contain a sulfonic group for every four polymer repeat units, while the more sulfonated samples (SPSU2B, SPSU3B) contain approximately one for every two. Elemental analysis confirms with high confidence the formation of silyl sulfonate polysulfone and the successive transformation into sulfonate products because the sum of the elements for every sample was close to 100%; i.e., no silane was present.

Besides the degree of sulfonation, the S/C ratio can be used to determine the IEC expressed as moles of sulfonated polymer repeat unit for 1 gram of dry polymer. To verify the accuracy of these results, IEC values for SPSU3 and Nafion 117 were measured by both the titration method and elemental analysis. Good agreement was found between the values as shown in Table I.

It was found that SPSU samples were soluble in polar aprotic solvents such DMAc, N,N-dimethylformamide, and dimethylsulfoxide, while they were insoluble in chlorohydrocarbons such as chloroform and dichloroethane.

An estimate of the molecular weight of PSU and SPSU samples was obtained using dilute solution viscosity measurements. It was found that the intrinsic viscosity increased with the sulfonation degree as reported in Table II. The results seem to confirm that this preparation method is suitable for producing ion-exchange materials with high molecular weight, without chain cleav-

Table I Elemental Analysis and Ion-Exchange Capacity for PSU and SPSU Samples

Polymer Sample	Reaction Conditions			Elemental Analysis						IEC Calculated ^d	IEC Measured ^e	
	X ^a	t ^b	T ^c	C	S	O	H	N	% SO ₃ H			
PSU				72.847	7.281	15.304	5.039					
SPSU1A	0.7	24	24–28	67.275	8.304	18.526	4.864	0.294	23.4	0.53		
SPSU1B	0.7	48	24–28	65.218	8.448	21.365	5.178	0.223	29.5	0.67		
SPSU2A	1.4	24	24–28	63.317	9.222	22.272	5.063		45.6	1.03		
SPSU2B	1.4	48	24–28	61.064	9.334	23.715	4.764	0.262	52.9	1.19		
SPSU3A	1.4	24	21–25	63.963	8.971	21.471	5.017	0.046	40.3	0.91	0.88	
SPSU3B	1.4	48	21–25	62.361	9.271	23.408	5.358		48.7	1.1	1.1	
Nafion 117										0.91	0.91	

^a mol sulfonating agent for mol of polysulfone.

^b Reaction time (h).

^c Mean room temperature during the day (°C).

^d IEC (mmol/g) by elemental analysis.

^e IEC (mmol/g) measured by titration.

age or side reactions. All the sulfonated samples have higher intrinsic viscosities (η_{int}) than the parent PSU, probably because the introduction of —SO₃H groups leads to enhancement of inter-chain interactions with a consequent higher resistance to the stretching of the main chains.

Thermogravimetric analysis results on PSU and SPSU with different sulfonation degree and Nafion 117 membranes are compared in Figure 1. The PSU is stable until 450–500°C; when decomposition of the main chain occurs, whereas SPSU and Nafion 117 membranes show several steps of weight loss. The first step at low temperature is due to the desorption of water bonded to the sulfonic groups. The second step, between 200 and 300°C, can be attributed to partial desulfonation; as proved by thermogravimetric studies connected to an infrared spectrometer or mass spectrometry (MS).^{23,24} Nafion 117 membrane shows a desulfonation temperature higher than SPSU, probably due to the difference in thermal stability of the C—S bond in perfluorocarbon group com-

pared to that of phenylene rings. The last step is connected to the polymer backbone decomposition. This temperature is higher for SPSU than Nafion 117 membranes, confirming the better thermal stability of the sulfonated polysulfone.

DSC analysis reveals higher glass transition temperatures (T_g) for SPSU samples with respect to PSU, although T_g values change with sulfonation degree. Thermal effects, likely due to desulfonation in the same range of temperature, do not allow evaluating the T_g value with accuracy. However, it was shown^{8,13,25} that the introduction of bulky groups in polymer chains produces steric hindrance to intersegmental motion reducing mobility and flexibility of the ether groups and increasing in T_g ²⁵ values. Moreover, the presence of electrostatic interactions between the ionic aggregates or clusters in ionomer membranes can further immobilize the polymer chains, producing an increase in T_g .

In Figure 2, the X-ray diffraction patterns for PSU and SPSU are reported. Typical broad bands

Table II Viscosity Values for PSU and SPSU Samples in DMA at 25°C

Polymer Sample	η_{rel}	η_{sp}	η_{red}	$\ln \eta_{\text{rel}}/c$	η_{int}
PSU	1.156	0.156	0.781	0.726	0.744
SPSU1A	1.214	0.214	1.070	0.970	1.002
SPSU1B	1.225	0.225	1.126	1.016	1.051
SPSU3A	1.326	0.326	1.631	1.411	1.411
SPSU3B	1.382	0.382	1.908	1.616	1.708

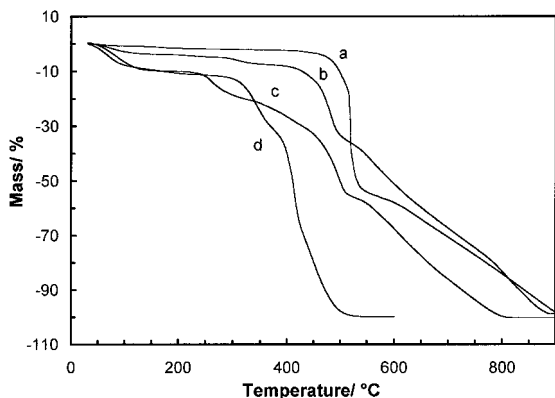


Figure 1 TGA thermograms of PSU, SPSU, and Nafion membranes, from 30 to 900°C in air. (a) PSU, (b) SPSU1A, (c) SPSU2B, and (d) Nafion 117.

of amorphous polymers without any crystallinity were found. A slight shift of the amorphous peak to higher angles was observed for highly sulfonated samples, corresponding to small changes in intersegmental spacing.

It is known from the literature^{26,27} that increases in water uptake of membranes is essential to improve conductivity. However, the water uptake of perfluorinated ionomer membrane depends on pretreatment of the membrane. Therefore, three cycles of drying and swelling of Nafion 117, SPSU3A and SPSU3B were carried out to verify the influence of this parameter. In the first cycle, the preswelled membranes were dried under vacuum (10^{-1} to 10^{-2} mbar) at 30°C for 18 h and rehydrated in water at different temperature between 25 and 100°C. In the second and third cycles, they were dried at 70°C for 18 h and rehydrated again under the same conditions. Notwithstanding the different treatments, the dry weight

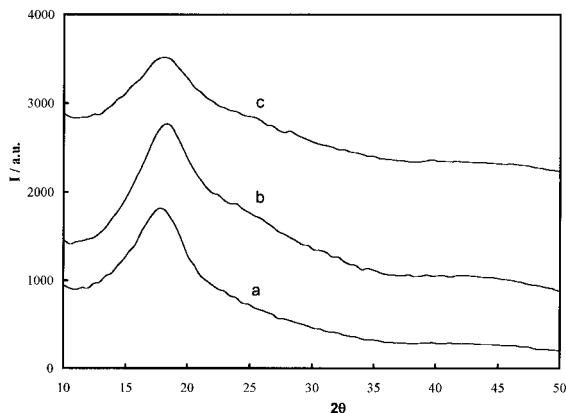


Figure 2 X-ray diffraction patterns of (a) PSU, (b) SPSU2A, and (c) SPSU2B samples.

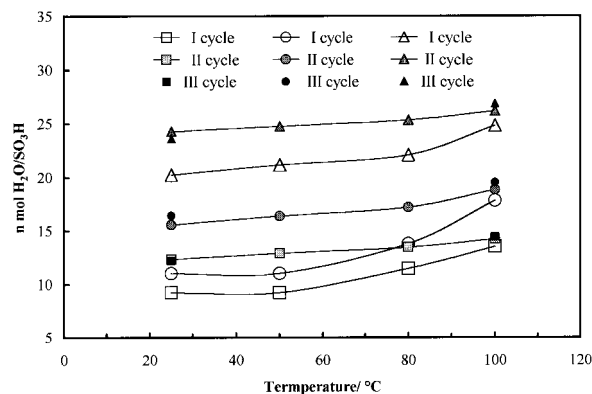


Figure 3 Water uptake in terms of number of water molecules with each SO_3H group ($n \cdot \text{H}_2\text{O}/\text{SO}_3\text{H}$) as function of the temperature: (\square) SPSU3A, (\circ) SPSU3B, and (\triangle) Nafion 117 membranes, in three different cycles.

was constant, while the wet weight was found to depend on the swelling temperatures with a remarkable increase in the first cycle at 100°C. Equilibrium in the water uptake was achieved by the second and third cycles. In Figure 3, the comparison between the water uptake of SPSU and Nafion 117 membranes is reported in terms of number of water molecules associated with each SO_3H group ($n \cdot \text{H}_2\text{O}/\text{SO}_3\text{H}$). This is the best method to compare ionomer membranes with different densities. At 100°C after the third cycle, a value of $17.2 n \cdot \text{H}_2\text{O}/\text{SO}_3\text{H}$ was found for SPSU3B. This value is not far from 25.3 obtained for Nafion 117 under the same conditions, although the latter value is slightly higher than that reported in literature.^{26–28} These results further confirm that ionomer membranes are history dependent and that extended water swelling is essential to maximize water uptake.

In Figure 4, IEC (from elemental analysis) and the specific proton resistance are reported as a function of the sulfonation degree. IEC linearly increases with the sulfonation degree while the specific proton resistance exponentially decreases from $5 \cdot 10^6$ to $10^2 \Omega \text{ cm}$. It is thought that even a small increase in sulfonic group concentration improves the membrane conductivity, due to smaller distances between ionic clusters, which favors proton migration through the membrane.

In Figure 5, proton conductivity of the SPSU3B membrane is compared with Nafion 117 as a function of temperature from 25 to 80°C. It can be seen that Nafion 117 is more conductive than SPSU3B in spite of its lower IEC. This behavior

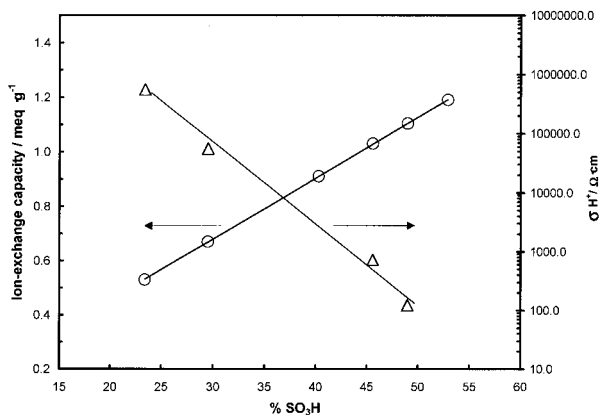


Figure 4 Ion-exchange capacity (\circ) and specific proton resistance (Δ) of sulfonated PSU membranes in dependence of sulfonation degree. Conditions of resistance measurements: $\nu = 1 \text{ kHz}$, $T = 25^\circ\text{C}$.

was reported by Kerrer et al.,¹⁴ and could be explained considering greater hydrophobicity and chains flexibility of Nafion backbone compared to that more rigid of the SPSU. Therefore, probably, there is a greater phase separation and then higher densities of sulfonic-water clusters and/or lower distance between clusters. Moreover, it is known that Nafion is a solid superacid catalyst,^{29,30} that has acid strength greater than that of 100% H_2SO_4 . Its superacidity is attributed to the electron-withdrawing effect of the perfluorocarbon chain acting on the sulfonic group, which favors the proton mobility.

Electrochemical Tests in H_2/O_2 Fuel Cell

Figure 6 shows the polarization behavior of SPSU2A, SPSU3B, and Nafion 117 membranes.

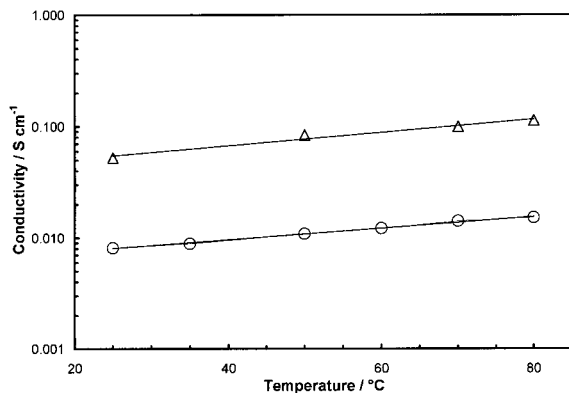


Figure 5 Proton conductivity of SPSU3B (\circ) and Nafion 117 (Δ) membranes as a function of the temperature.

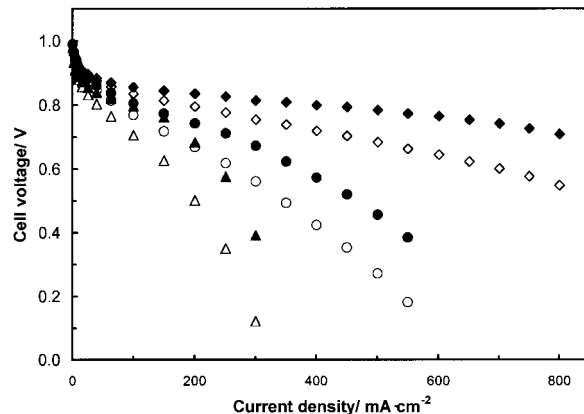


Figure 6 Cell voltage vs current density for MEA of (Δ) SPSU2A, (\circ) SPSU3B, and (\diamond) Nafion 117 membranes. Black symbols for ohmic resistance free curves. Fuel cell test conditions: $T_{\text{cell}} = 80^\circ\text{C}$; $P_{\text{H}_2} = 3 \text{ bar abs.}$; $P_{\text{O}_2} = 3 \text{ bar abs.}$

A remarkable difference in the cell performance is evident, which, however, cannot be attributed only to different conductivities. In fact, if we eliminate the membranes resistance by subtracting material ohmic resistance from polarization data (iR free curves in Fig. 6) there are no superpositions in the curves. It means that other factors affect SPSU performance as the poor electrode/electrolyte contact caused from the assembly of a nonperfluorinated membrane with a catalytic layer containing Nafion ionomer and the low chains mobility of these glassy polymers. Then a beneficial effect can be obtained replacing the Nafion with the SPSU ionomer in the catalytic layer and decreasing the T_g value with the addition of a suitable plasticizer³¹ during the preparation. In any case, a slight increase in sulfonation degree from 45% in SPSU2A to about 50% in SPSU3B produces a considerable improvement in MEA performance.

CONCLUSIONS

Ion-exchange membranes of SPSU were prepared following a new sulfonation process. This method does not produce degradation of chains during sulfonation as revealed from intrinsic viscosity values.

X-ray diffraction patterns show amorphous structures for both PSU and SPSU membranes, and only small structural arrangements with the increase of the sulfonic groups.

The glass transition temperature (T_g) increases in the sulfonated membranes and a desulfonation process occur at 200–300°C before complete polymer decomposition.

SPSU membranes show IEC from 0.5 to 1.2 mmol $\text{SO}_3\text{H/g}$ and proton conductivity between 10^{-6} and 10^{-2} S cm^{-1} , depending of the sulfonation degree.

A lower water uptake capacity and proton conductivity were found for SPSU respect to Nafion membranes with the same IEC. This behavior was attributed to greater densities of sulfonic-water clusters and/or lower distance between clusters.

From electrochemical tests in a fuel cell encouraging results were obtained for the use of SPSU membranes in this application even if the performance remains lower than Nafion. Besides to the low proton conductivity, a poor contact electrode/electrolyte appears to be the main cause. An improvement could be obtained replacing the perfluorosulfonic ionomer in the catalyst layer with the sulfonated polysulfone and lowering the high T_g of the polymer.

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