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# Crosslinked Sulfonated Polysulfone-Based Polymer Electrolyte Membranes Induced by Gamma Ray Irradiation

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Sulfonated aromatic polymers generally show high swelling at high proton conductivity. This disadvantage makes many of them unfit for proton exchange membrane applications. Crosslinking of the polymer is one way to overcome this problem. In this study, radiation-induced crosslinking was performed on a sulfonated polysulfone membrane, with doses ranging from 2.5 to 25.0 kGy (dose rate: 45 Gy/min) using gamma rays from a <sup>60</sup>Co source. The pristine sulfonated polysulfones was obtained by mild sulfonation of bisphenol-A-polysulfone with trimethylsilyl chlorosulfonate as sulfonating agent. The proton conductivity of the membranes was characterized by means of electrical impedance spectroscopy techniques. Ion-exchange capacity, degree of sulfonation, water content and chemical stability membrane properties were characterized before and after irradiation. The results show that the mechanical, chemical and thermal stability of the membrane improve after irradiation. The degree of sulfonation and the proton conductivity exhibit a tendency to decrease with increasing irradiation total dose.

**Keywords** crosslinking, membrane, polymer electrolyte, radiation, sulfonated polysulfone

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## INTRODUCTION

Humanity lives, today, at the end of an era characterized by the extensive use of fossil fuels, leading to environmental pollution and consequent change in the planet climate. Factors like this, besides the future decline of oil production, in addition to the geopolitical instability and the growing global energy demand, result in the need to reduce the oil dependency of energy production. Fuel cells have been given great attention as new energy conversion technologies for their promising applications in new clean power sources. The fuel cell is also more efficient in its conversion of chemical energy to electrical energy than present technologies [1]. Among the technology types of fuel cells, the proton exchange membrane fuel cell has been receiving great attention due to its highly attractive properties as power sources for both stationary and mobile applications [2,3]. Polymer electrolyte membranes play an important role in the development of the fuel cell technology. The Nafion<sup>®</sup> type membrane, produced by DuPont, is the most widely used electrolyte in polymer electrolyte fuel cell (PEFC) due to its high proton conductivity, and mechanical, chemical and electrochemical stability. However, this type of membrane also exhibits some drawbacks, mainly the limit of operation temperature to below 100°C. As a consequence, there are many efforts to find alternatives to these perfluorinated membranes [4,5,6]. Polysulfones are known for their high thermal, chemical and mechanical stability. Polysulfones can be modified by chemical sulfonation to become an ionomer, a polymer with sulfonic groups in the backbone [4,7,8]. To achieve good proton conductivity, polysulfone must be highly sulfonated. As a result, these polymers swell substantially with water uptake and some are even soluble in water. Crosslinking may be employed to decrease the water swelling of these membranes and improve the mechanical strength but results in decreased proton conductivity [9]. High-intensity gamma ray is absorbed in a polymer and the solvent by interaction with the valence electrons of the atoms, which induced the breaking of chemical bonds producing a free radical, a reactive species having a single unpaired electron, ions and excited states. The chemical changes in the polymer result from the reactions of these species formed in polymer (direct action) and in the solvent (indirect action). The molecular changes occurring in polymers as a result of radiation-induced chemical reactions may be classified as: 1) chain cross-linking effecting an increase in molecular weight and formation of a macroscopic network; 2) chain scission effecting a decrease in molecular weight and formation of volatile molecules; 3) formation of new chemical bonds, and (4) chemical reactions with chemical atmosphere such as oxidation. These four events can, in turn, lead to membrane microstructure and property alterations [10].

In this paper, we prepared sulfonated bisphenol-A-polysulfone (SPSF) samples, with a degree of sulfonation (DS) between 46 and 83%, by homogeneous method. The SPSF membranes were fabricated using dimethylacetamide as casting solvent. Radiation-induced crosslinking was performed on the SPSF films after sulfonation, using gamma ray from a  $^{60}\text{Co}$  source. The properties of the crosslinking SPSF membranes were evaluated with respect to the fuel cell applications [2].

## EXPERIMENTAL

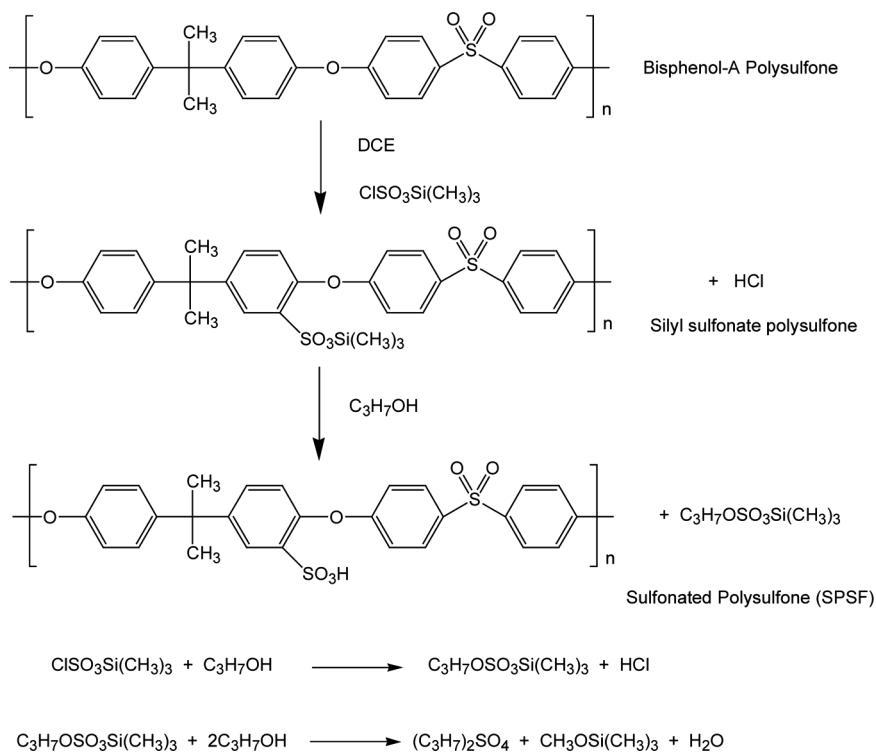
### Materials

Bisphenol-A-polysulfone (PSF) ( $M_w = 60.000$ ,  $T_g = 187^\circ\text{C}$ ,  $D = 1,24$ , Ultrason<sup>®</sup> 56010) was kindly provided by BASF. The polymer was dried in vacuum oven at  $100^\circ\text{C}$  for 24 h prior to use. Trimethylsilyl chlorosulfonate [ $(\text{CH}_3)_3\text{SiSO}_3\text{Cl} - \text{TMSCIS}$ ] (assay  $\geq 99\%$ ) was purchased from Aldrich and used without further purification. The solvent used for membrane casting, *N,N*-dimethylacetamide (DMAc) for synthesis (assay  $\geq 99\%$ ), was purchased from Merck. All others chemical obtained commercially were reagent-grade and used as received.

### Sulfonated Bisphenol-A-Polysulfone (SPSF)

The sulfonated polysulfone was synthesized using trimethylsilyl chlorosulfonate as the sulfonating agent (SA) in a 1,2-dichloroethane (DCE) homogeneous solution (Figure 1). TMSCIS was chosen as the sulfonating agent because it is among the less aggressive reagents [11]. The sulfonation procedure is an example of an ionomer obtained by the chemical modification of a commercial thermoplastic [12]. This chemical modification of polymers results in functional groups perfectly distributed along the macromolecular backbone.

The reaction was conducted in a glove box with humidity control (below 10 ppm). The mixture of DCE and TMSCIS was added dropwise to the above PSF solution. The system was kept under magnetic stirring, heating, and argon flux to remove the HCl formed during the reaction. After the reaction time, the material obtained was precipitated in freezing isopropyl alcohol, under mechanical agitation. Thus, the polymer precipitated was obtained in acid form. The precipitate was washed with isopropyl alcohol to remove the residual acid. Subsequently, the polymer was dried in a vacuum oven (5 mm Hg) at  $80^\circ\text{C}$  for 24 h. The sulfonation degree was controlled by the molar ratio of the sulfonation agent and the polymer repeating unit, reaction time and temperature [13,14].



**Figure 1:** Sulfonation of PSF by trimethylsilyl chlorosulfonate (TMSCIS) (9).

## Membrane Preparation

The membrane was prepared from 20% SPSF homogeneous solutions in *N,N*-dimethylacetamide (DMAc). The polymer was kept 8 h in contact with the solvent and dissolution was completed with mechanical stirring at 60°C temperature. The membrane was afterwards prepared by casting of the SPSF solution on a glass plate and the solvent was slowly evaporated at moderate temperature (about 60°C) for 24 h. Subsequently, the membrane was peeled off the glass with the help of distilled water. To ensure complete solvent removal, the membranes were placed under vacuum at 80°C for an addition 48 h. Membranes of 100 μm thickness were obtained [7,8,12,15].

## Ion-Exchange Capacity (IEC) and Degree of Sulfonation (DS)

The degree of sulfonation (DS) is defined as the number of  $-\text{SO}_3\text{H}$  groups per repeating monomer unit, and ion-exchange capacity (IEC) as the milliequivalents of  $\text{H}^+$  per weight of dry SPSF membrane. Initially, the membrane was

equilibrated in 0,1 N HCl solutions for 24 h to convert the membrane into H<sup>+</sup> form. After that, the membrane was washed with deionized water to remove excess of free HCl [2,7]. Then it was equilibrated in saturated NaCl solution for 24 h at 60°C and IEC was determined from increase in acidity, which was determined by acid-base titration with standard NaOH solution. The titration results have been used to calculate both the ion exchange capacity (Eq. (1)) and degree of sulfonation (Eq. (2)):

$$\text{IEC} = (C_{\text{Na}}^+ \times V_{\text{NaOH}}) / W_{\text{d}} \quad (1)$$

where  $C_{\text{Na}}^+$  is the concentration of Na<sup>+</sup> in the tritant solution,  $V_{\text{NaOH}}$  is the NaOH solution volume used to neutralize and  $W_{\text{d}}$  is the dried membrane weight [16,17]:

$$\text{DS} = (442 \times \text{IEC}) / [1 - (80 \times \text{IEC})] \quad (2)$$

where 442 is the molecular weight of the PSF repeat unit and 80 the molecular weight of the  $-\text{SO}_3^-$  group.

## Irradiation Crosslinking

The SPSF films were cut into pieces and dried in a vacuum oven at 80°C. The dried films were precisely weighed and immersed in deionized water in a glass reactor. The solution was bubbled with dried nitrogen for 5 min at a flow rate of 10 l/h to remove all oxygen in the vessel and create an inert atmosphere. After that, the reactor was closed with sealing material. The irradiation crosslinking makes the SPSF films insoluble in deionized hot water, and enhances the mechanical, dimensional and chemical stabilities of the resultant polymer electrolyte membranes. Radiation crosslinking of the SPSF films was performed at room temperature under atmospheric air using a MDS Nordion model Gammacell 220 Excel gamma. The determined irradiation dose rate was 45 Gy/min, and the irradiation time was calculated considering the irradiation total dose and dose rate [18]. After irradiation, the SPSF films were thermally treated in a vacuum oven at 120°C for 8 h for quenching any residual radicals [2]. The membrane sulfonation degree was determined before and after irradiation by acid-base titration [19].

## Water Content (WC)

The swelling properties of the membranes were obtained by water content measurements. Initially, protonated membranes were dried under vacuum (5 mm Hg) at 120°C of temperature until constant weight. They were then immersed in deionized water at 40°C for 24 h. The water content percentage was calculated as the ratio of the weight of water gained during the immersion

to the weight of the membranes in their dry state using the Eq. (3):

$$\text{water content (\%)} = (W_h - W_d)/W_d \quad (3)$$

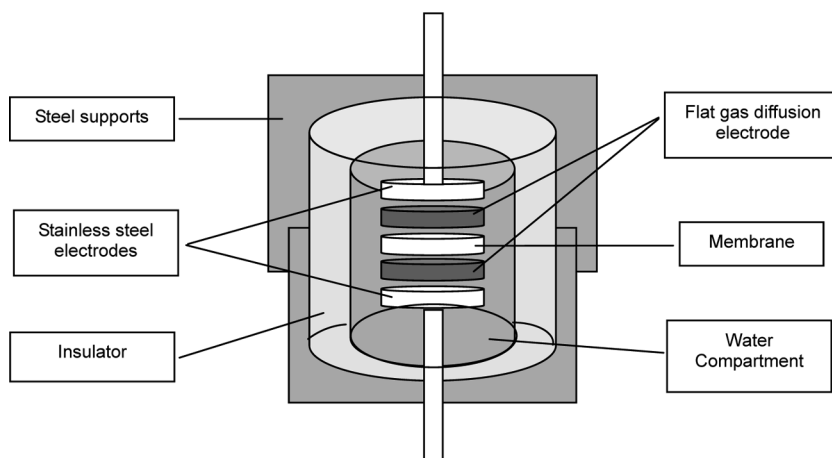
where  $W_h$  and  $W_d$  are the weight of wet and dry membranes, respectively [3,7].

## Membrane Conductivity Measurements

The electrical impedance spectroscopy (EIS) method involves measuring the impedance as a function of the frequency of the applied signal over a wide frequency range, typically 10 Hz to 1 MHz [20]. One of the most important features of EIS comes with the development of a direct correlation between the response of a real system and an idealized model circuit composed of discrete electrical components. The representation of impedance is analogous to the representation of a complex number, which can be separated into real and imaginary parts by algebraic rules. Analysis of the impedance data is often carried out by the complex method using the Nyquist plot [21].

In this work, the proton conductivity ( $\sigma$ ) of the membranes was measured in the transversal direction using a potentiostatic two-electrode mode with alternating current (a.c.) in an electrochemical cell. The cell is composed of two 1.0 cm<sup>2</sup> effective area stainless steel electrodes. The membrane was sandwiched by flat gas diffusion electrode (E-TEK<sup>®</sup> Electrode) and tightly clamped by the stainless steel electrodes (Figure 2). The cell has a provision compartment of water to maintain the membrane humidity.

Prior to the conductivity test, the membrane was equilibrated in 0.1 N HCl solution at 80°C for 1.0 h and then washed and stored in deionized water. Impedance analysis was recorded in a thermostatic cell at 30 and 80°C of



**Figure 2:** Conductivity measurement electrochemical cell.

temperature, with an oscillation potential of 10 mV over the frequency range of 10.00 Hz to 1.00 MHz. The Autolab PGSTAT 30 (Eco Chemie B. V., Netherlands) with frequency response analysis (FRA) software was used for data treatment. The real impedance taken at zero imaginary impedance was used to calculate the proton conductivity of the membrane [22]. There are many uncertainties on conductivity measurements related to the cell calibration (electrode surface area, membrane thickness and hydration). Due to these uncertainties the conductivity measurements error is greater than 20% [23]. The proton conductivity of membranes was determined using the Eq. (4):

$$\sigma = L/RA \quad (4)$$

where  $\sigma$  is the proton conductivity, L the membrane thickness, R the membrane resistance obtained from impedance analysis, and A is the membrane area.

## Chemical Stability - Fenton's Test

As it has been recognized that the formation and reactivity of free radical peroxide species are a major source of degradation of PEMs used in fuel cells, the Fenton's test, using a  $H_2O_2$  solution containing a trace amount of  $Fe^{2+}$ , has become a common *ex situ* accelerated test for membrane durability. Membranes of 100  $\mu m$  of thickness were cut into pieces (1,5 cm  $\times$  1,5 cm) and immersed in Fenton's reagent (3%  $H_2O_2$ /2 ppm  $Fe^{2+}$ ) at 80°C of temperature. The chemical stability of the samples was characterized by the elapsed time that the membrane started to dissolve and dissolved completely in the solution [6,17,22].

## RESULTS AND DISCUSSION

### Sulfonation Reaction

The degree of sulfonation obtained depends on materials and reaction conditions, including the sulfonation agent, solvent, reaction time, reaction temperature and polymer concentration. For a determined sulfonation agent and polymer concentration, sulfonation was carried out by varying parameters such as mole ratios of the sulfonation agent to the polymer repeat units, solvent, temperature and reaction time. The achieved DS, determined by titration, varied from low to high enough that it can be dissolved in deionized water at 60°C (SPSF12). The reaction conditions, DS and chemical stability are presented in Table 1. The SPSF12 has the double mole ratio of the sulfonation agent to the polymer repeat units than the SPSF06 sample and the same other reaction conditions. As can be seen, the DS obtained for SPSF12 is



**Table 1:** Reaction conditions of PSF sulfonation. Mole ratios of the sulfonation agent to the polymer repeat units (X), solvent, temperature (T), time, yield, degree of sulfonation (DS), ion exchange capacity (IEC), proton conductivity ( $\sigma$ ) and chemical stability (CS) of the SPSF membranes.

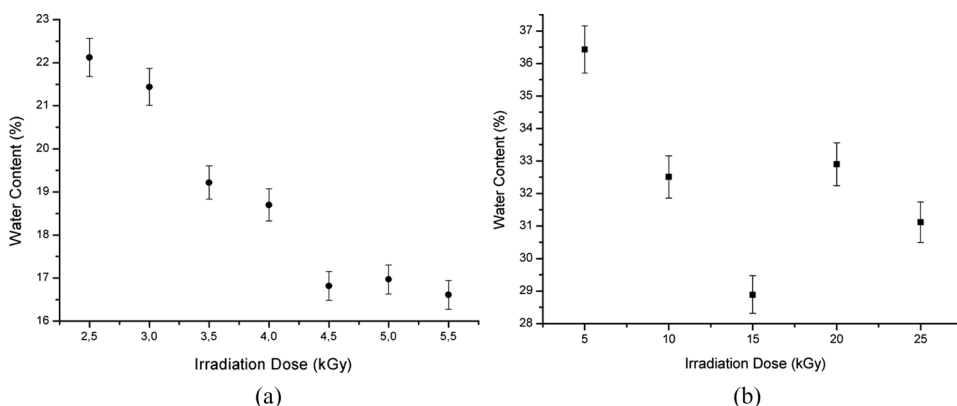
Sample	X	Solvent	T (°C)	Time (h)	Yield (%)	DS	IEC meq/g	$\sigma$ (mS/Cm) 30°C	CS (min)
SPSF05	1,35	DCE	40,0	5,0	89,00	70,6	1,416	33	80
SPSF06	1,00	DCE	50,0	5,0	83,90	54,7	1,126	20	90
SPSF07	1,35	DCE	25,0	5,0	95,30	46,0	0,961	6	150
SPSF08	1,35	DCE	70,0	5,0	87,60	75,2	1,498	31	78
SPSF09	1,35	CHCl <sub>3</sub>	50,0	5,0	99,00	46,7	0,974	20	130
SPSF10	1,35	DCE	50,0	6,0	81,97	73,7	1,471	72	98
SPSF11	1,35	DCE	50,0	24,0	83,39	75,0	1,494	78	38
SPSF12	2,00	DCE	50,0	5,0	84,40	83,4	1,639	90	10

higher than the SPSF06 sample. But the SPSF12 sample is very unstable and shows an irreversible drastic swelling in hot water, resulting in a gel-like state with a limited lifetime in the electrolysis system, while the SPSF06 sample resists till 90°C in deionized water. This was probably due to possible chain scission during the electrophilic substitution [9,23]. Prior study by Iojoiu and coworkers [12] about intrinsic viscosities showed that even using the less aggressive reagent (TMSCIS) may lead to chain breaking as a function of the argon flow used during the reaction. The chain breakage and consequently the intrinsic viscosities reduction are induced by the HCl by-product of the sulfonation reaction.

The effect of temperature on the sulfonation is of prime importance. Usually increasing the reaction temperature increases the rate of sulfonation, but decreases polymer molecular weight by chain scission. The only difference between SPSF05, SPSF07 and SPSF08 samples is the reaction temperature, 40, 25 and 70°C, respectively. As can be seen in Table 1, the DS increase with the increasing reaction temperature. The SPSF07 sample showed better chemical stability but lower DS. This behavior could be attributed to the less energetic characteristics of the reaction (activation energy, collision frequency factor) as a function of the lower temperature. Due to chemical stability and elevated DS, the samples SPSF08 and SPSF10 showed the best reaction conditions to obtain membranes for PEFCs purposes.

## Water Content and Chemical Stability

Proton conductivity and mechanical stability are strongly affected by the presence of water in membranes. When hydrated, the hydrophilic part of membranes provides good proton conductivity. The main chain of the



**Figure 3:** Water content as a function of irradiation total dose of (a) SPSF06 and (b) SPSF08 membrane.

polymeric membranes, the hydrophobic part, provides good morphological and mechanical stability. So, controlling polymer membranes with appropriate levels of water content is very important [24]. The water content of the membranes is related to the irradiation total dose. Figures 3a and 3b show the water content variation of SPSF06 and SPSF08 samples, respectively. As can be seen, the WC decreases with increasing in the irradiation total dose, in both cases.

The chemical, or oxidative, stability of the irradiated SPSF membranes was investigated by observing the dissolution in Fenton's reagent. Tables 2 and 3 show the chemical stability increasing with irradiation total dose while decreasing DS of the SPSF06 and SPSF08 samples, respectively. The excellent chemical stability of PSF polymer may be attributed to the rigid molecular structure of the phenyl rings. The PSF sulfonation introduces strong polar sulfonic groups in the polymer chain, which damage the ordering of the

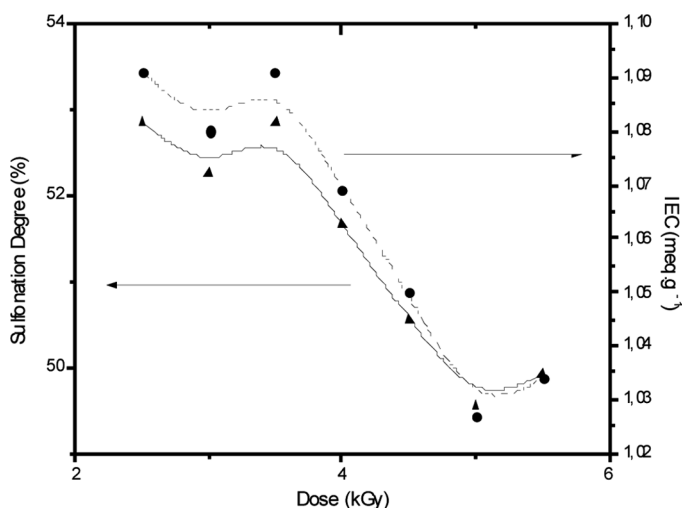
**Table 2:** Degree of sulfonation (DS), water content (WC), proton conductivity ( $\sigma$ ), ion exchange capacity (IEC), chemical stability (CS) and thickness of the SPSF06 membranes obtained with different irradiation doses.

Dose (kGy)	DS (%)	WC (%)	$\sigma$ (mS/Cm) 30°C	IEC (meq/g)	CS (min)	Thickness ( $\mu\text{m}$ )
2.5	52.85	22.12	23.1	1.091	90	106
3.0	52.25	21.44	15.0	1.080	95	110
3.5	52.84	19.22	22.5	1.091	89	108
4.0	51.66	18.70	21.0	1.069	105	109
4.5	50.56	16.82	20.5	1.050	111	107
5.0	49.55	16.97	17.2	1.027	120	105
5.5	49.92	16.61	10.0	1.034	118	108

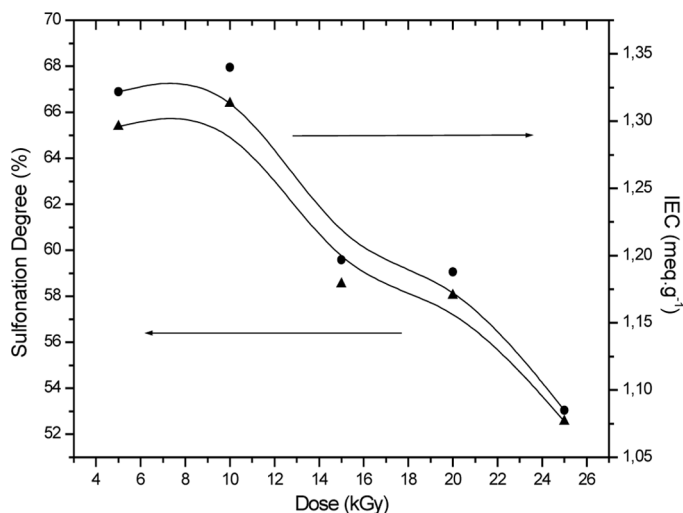
**Table 3:** Degree of sulfonation (DS), water content (WC), proton conductivity ( $\sigma$ ) at 30 and 80°C temperature, ion exchange capacity (IEC), chemical stability (CS) and thickness of the SPSF08 membranes obtained with different irradiation doses.

Dose (kGy)	DS (%)	WC (%)	$\sigma$ (mS/Cm)		IEC (meq/g)	CS (min)	Thickness ( $\mu\text{m}$ )
			30°C	80°C			
5	65.38	36.43	99,0	58,5	1.322	80	115
10	66.38	32.51	95,2	99,2	1.340	87	109
15	58.54	28.89	63,8	67,2	1.197	92	118
20	58.04	32.90	44,1	50,0	1.188	95	108
25	52.56	31.12	27,7	35,7	1.085	110	120

polymer chains, thus decreasing the chemical stability [17,25]. When the SPSF06 and SPSF08 membranes are irradiated, some of the sulfonic-benzene ring bonds are broken, a positive radical on the benzene ring is formed and  $\text{H}_2\text{SO}_4$  is released. The free radical on the benzene ring is hypothesized to bind to an unbroken free sulfonic site to increase crosslinking and decrease the sulfonation degree and IEC. The relation of DS and IEC as a function of increased total irradiation dose of the SPSF06 and SPSF08 samples are shown in Figures 4 and 5, respectively. The degree of sulfonation and the ion change capacity decreases proportionally while the chemical stability tends to increase with increasing the irradiation total dose.



**Figure 4:** Degree of sulfonation (▲) and IEC (●) as a function of irradiation total dose of irradiated SPSF06 membranes.



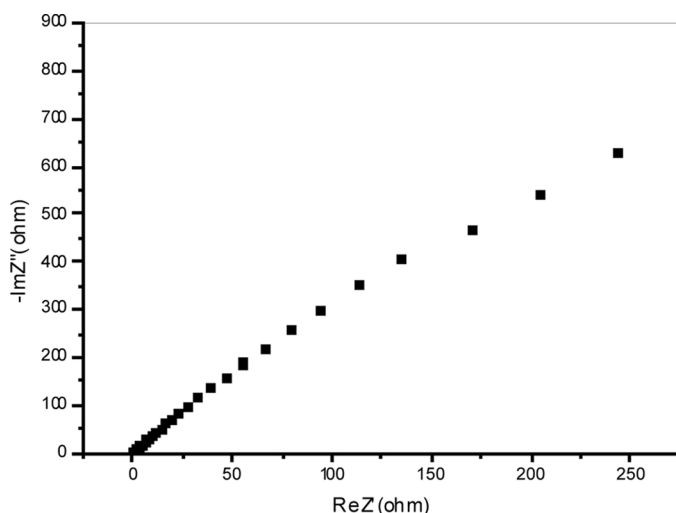
**Figure 5:** Degree of sulfonation (▲) and IEC (●) as a function of irradiation total dose of irradiated SPSF08 membranes.

## Proton Conductivity

The proton conductivity of irradiated SPSF membranes in the transversal direction was measured at 30 and 80°C in hydration conditions and the results are shown in Tables 2 and 3. The proton conductivity exhibits a tendency to decrease with increasing irradiation total dose. The conductivity results of the irradiated SPSF08 sample are greater than the SPSF06 sample. These results are expected as a function of the degree of sulfonation and water content of the SPSF membranes. When irradiated, the hydrophilic ionic clusters of the SPSF membranes decrease with crosslinking formation. At lower DS, the sulfonic groups are segregated, which results in low conductivity. When sulfonic groups become continuous to form interconnecting channels, the proton transport is facilitated and conductivity increases [17].

The accurate determination of proton conductivity of SPSF membranes is essential to be used in PEFCs. However, the high conductivity values, and their dependence on relative humidity (RH), create uncertainties in measurement, and the literature reports different values for Nafion<sup>®</sup> proton conductivity in the same experimental conditions. The internal humidification control of the membrane in the electrochemical cell during the conductivity measurement is very difficult. The conductivity measurement at a temperature of 80°C is greater than at a temperature of 30°C (Table 3). Nyquist plot obtained at 80°C temperature of 20,0 kGy irradiated SPSF08 membranes in wet state is shown in Figure 6.

The impedance of the polymer electrolyte membrane system was constant at high frequencies, corresponding to the conductivity of the membrane [20].



**Figure 6:** Nyquist plot measured at 80°C of 20,0 kGy irradiated SPSF08 sample (IEC = 1,18 meq/g).

The resistance of the membrane is taken on the real axis at the minimum of the imaginary part of the Nyquist plot [12]. The membranes were pressed between two E-TEK<sup>®</sup> Electrodes to decrease the mass transfer resistance between the membrane and the cell electrodes. The evaluation of the cell resistance was performed subtracting the E-TEK<sup>®</sup> Electrodes effect. The increased number of sulfonic groups incorporated into the sulfonated samples greatly enhanced the water uptake by the membrane matrix, reducing its electrical resistance [21].

## CONCLUSIONS

In this study, sulfonation of polysulfone was performed in a homogeneous solution with trimethylsilyl chlorosulfonate (TMSCIS) as the sulfonating agent and DCE as the solvent. A series of SPSF samples with different DS was prepared and characterized. Membranes prepared from SPSF showed increased swelling and decreased chemical stability as DS increased. The radiation crosslinking makes the SPSF films insoluble in water, and enhances the mechanical, dimensional and chemical stabilities. The crosslinked SPSF membranes were prepared at room temperature under atmospheric air by gamma ray irradiation at different total doses. The final result depends on the nature of the material and the irradiation conditions. The increased chemical stabilities and decreased water content of SPSF membranes suggest that crosslinking is the predominant reaction in the irradiated sulfonated

membrane. The results showed that the crosslinking increase by the irradiation does not affect seriously the proton conductivity of the membranes. When using irradiation crosslinking to enhance membranes' mechanical properties, the control of sulfonation protocol synthesis is very important to avoid chain scission of the polymers. The irradiated SPSF membranes are easy to prepare and less expensive than the commercial Nafion<sup>®</sup> membranes. Their high conductivity permits them to be considered for using in PEFC applications [26,27].

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