

**Properties of Polystyrene/Acrylic acid membranes after sulphonation reactions**

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**ABSTRACT**

Sulphonation reaction in styrenic membranes is a common method used to graft ionic groups needed to enhance proton conductivity in polymeric electrolytes. A synthesized copolymer of styrene and acrylic acid (94/6 % mol) crosslinked with a tryfunctional monomer TMPTMA (0.01 % mol) was used as a PEM membrane system for sulphonation reactions. Such copolymer was sulphonated with sulphuric acid (98%) at 50, 75 and 100 % molar ratio considering styrene rings and during 1 and 2 hours of reaction time. FTIR spectra were obtained to observe chemical groups in the materials, TGA thermograms for thermal stability and DMA to evaluate mechanical effects after sulphonation reactions. Water absorption and its effect on proton conductivity by means of EIS were also evaluated. FTIR spectra show characteristic bands corresponding to sulphone groups, while sulphonating agent concentration and/or sulphonation time induce higher glass transition temperatures and no changes in thermal stability. Latter condition also allows higher water absorption and an enhancement in proton conductivity.

**1. Introduction**

Perfluorosulphonic acid membranes (Nafion) is the most convenient membrane to use into a PEMFC nowadays, basically due to the ionic active sulphonic groups. According to the latter, alternative materials search for cheap polymeric materials treated with sulphonation reactions to graft such groups and increase their ionic activity to be able to use them as a polyelectrolyte into a fuel cell. Alternative membranes can be divided in 3 groups: modified prefluorosulphonic acid membranes, acid-base complex membranes and alternated sulphonated hydrocarbon polymers [1]. The last group involves several systems as well as preparation methods and is usually of very low cost with an important variety of common materials to find. They also have high water absorption in a wide temperature range and easily recyclable. [2]

Such membranes can be prepared by polymerization or copolymerization reactions of monomers containing anionic or cationic radicals; otherwise such radicals can be introduced into the polymer through chemical reactions or by functional group grafting reactions. For the latter, sulphonation reactions is one of the most common methods, where

for the case of polystyrene, an aromatic electrophilic substitution is carried out and a hydrogen atom is changed by a sulphonic acid group [2-4].

A research group [3] studied the mechanical behavior and ionic conductivity of a sulphonated poly(aryletherketone) bifenilate at several sulphonation times. They found excellent mechanical properties, high dimensional stability and ionic conductivity for a degree of sulphonation of the unity ( $DS=1$ ) for a reaction time of 3 hours and evaluated at 80 °C. On the other hand, Sherazi et al [5] crosslinked UHMWPE with styrene and prepared membranes by press molding to then sulphonate them with chlorosulphonic acid. They obtained membranes with high proton conductivity and lower permeability to methanol than Nafion.

Another easy two-step method with lower cost is the copolymerization of styrene-divinyl benzene and further sulphonation reaction with concentrated sulphuric acid [6]. Moreover, Deb and Mathew [7] reported the characteristics of sulphonated styrene-acrylic acid copolymers, they experimented with styrene levels of 47-55 % mol. According with their results, such materials are useful as pH sensors as well.

Paula et al [8] reported the synthesis of different molar ratios of poly(styrene-acrylic acid) copolymers through radical polymerization at 110 °C during 2 hours and then sulphonated at 40 °C during 90 minutes. The 92:8 molar ratio copolymer showed high conductivity values for different moisture content.

Our research group has been preparing copolymers of styrene and acrylic acid at different ratios and with different levels of crosslinking to enhance mechanical properties, however, sulphonation procedure is a basic step to control during membrane preparation, since such groups will define the conductivity properties of the final material.

## **2. Experimental**

### Synthesis of crosslinked copolymers

A 100 ml glass reactor was loaded with styrene and acrylic acid in a 94:6 molar ratio, TMPTMA crosslinking agent (trimethylol propane trimethacrylate) was also added at the concentration of 0.01 % mol. Radical copolymerization was carried out using benzoyl peroxide (0.05 % mol) as initiator and keeping reactor temperature at 100 °C, under nitrogen atmosphere and mechanical stirring (250 rpm) during 2 hours. The copolymer was dissolved with acetone and the solution precipitated with methanol; the latter procedure was repeated twice in order to eliminate low molecular weight material and the solid dried overnight and then into a vacuum oven. The percent of copolymerization yield reached 38%.

### Sulphonation of copolymers

The copolymer was sulphonated in a similar reactor used for the synthesis, using about 2 g of the copolymer dissolved in 30 mL of dichloromethane at room temperature and 250 rpm of stirring. Once the material dissolved completely, the system was heated to 40 °C before adding the sulphuric acid. The amount of aromatic rings was

calculated and the acid added to cover 50, 75 and 100 %mol of such rings. Sulphonation reaction time was also controlled to have 1 and 2 hours and the procedure finished adding 100 mL of cold distilled water (kept previously into an ice bath). Expected crosslinked and sulphonated chemical structure is shown in Figure 1.

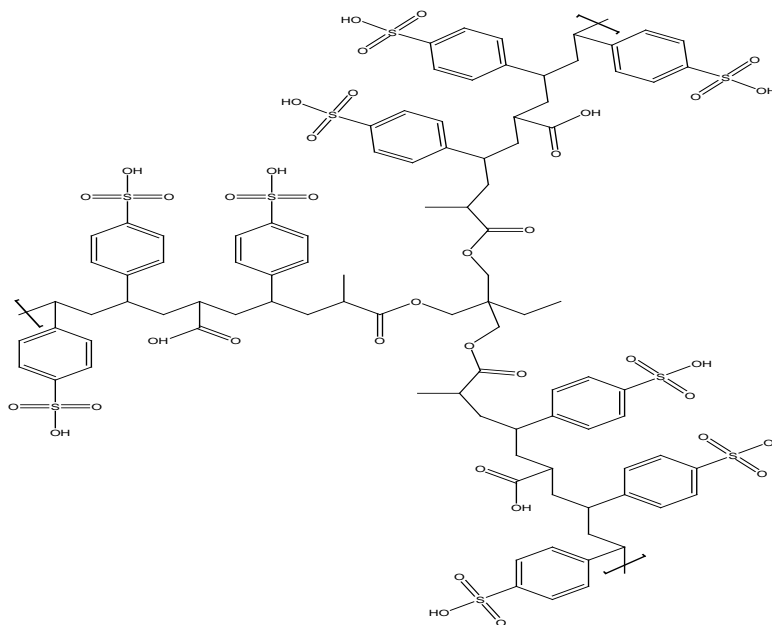


Figure 1. Proposed structure for the sulphonated copolymer

#### Characterization of copolymers

An aliquot of each copolymer (0.02 g) was dissolved with THF (1 ml) and the solution deposited in a flat confined glass plate in order to have films of approximately 0.03 mm thickness after solvent evaporation (casting). FTIR spectra of the films were recorded in a Nicolet Avatar 330 instrument. 64 scans and a resolution of  $4\text{ cm}^{-1}$  were used. TGA thermograms were carried out in a Q500 TA Instruments apparatus. Approximately 20 mg of sample was placed into the thermobalance and evaluated from ambient up to  $700\text{ }^{\circ}\text{C}$ , with a  $10\text{ }^{\circ}\text{C}/\text{min}$  thermal ramp under nitrogen atmosphere. Mass loss was recorded along temperature.

Dynamic mechanical properties were evaluated by means of a DMA TA Instruments Q800. A tension accessory was used for deformation, with amplitude of 20 microns and a frequency of 1 Hz in the temperature range of ambient to  $130\text{ }^{\circ}\text{C}$  with a ramp of  $5\text{ }^{\circ}\text{C}/\text{min}$ .

Capacity of water absorption was obtained gravimetrically obtaining their weight in dry and after 24 hours of being immersed into a  $0.05\text{ M H}_2\text{SO}_4$  solution, washed thoroughly with ultra pure water and immersed again in such water.

Electrochemical properties of sulphonated copolymers were obtained with a potentiostat/galvanostat BioLogic SP-300, using the technique of electrochemical impedance spectroscopy (EIS). The potentiostat mode was used in the frequency range of 2-30 MHz and the open circuit potential, collecting 10 points by decade. Measurement was carried out with a two electrode system with platinum strip as electrode supporting the membrane in one side and a hole full of mercury with a platinum wire in the other side. Distance between inferior and superior sides was kept constant for all measurements (30.82 mm).

### 3. Results and discussion

Infrared spectroscopy is a very useful technique to evaluate the addition of sulphonic groups into the copolymer. Figure 2 shows the spectra for the crosslinked material with 0.01 % TMPTMA and sulphonated at different levels and time.

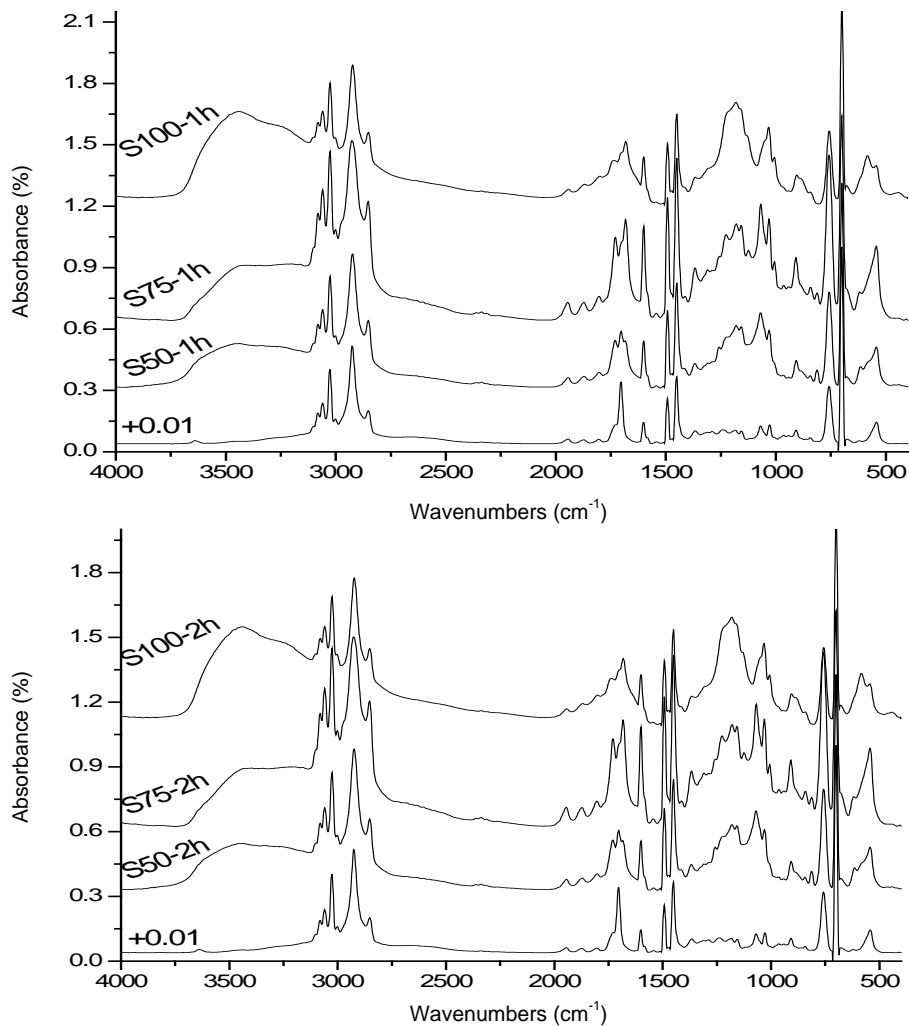


Figure 2. FTIR spectra of copolymer sulphonated at 50, 75 and 100 % mol at 2 reaction times (1 and 2 hours)

Many important differences can be seen for non and sulphonated copolymers, the most noticeable is the formation trend of a wide and strong band at  $3500\text{--}3100\text{ cm}^{-1}$ , which is a strong indication of the  $\text{SO}_3\text{H}$  group addition since it corresponds to the absorption of the OH from the sulphonic group. A similar band was also reported by Proença [9] for membranes of sulphonated polystyrene and polyaniline.

Another spectra region showing differences after sulphonation is between  $1400\text{--}1000\text{ cm}^{-1}$ , corresponding to the  $\text{SO}_2$  asymmetric stretching ( $1390\text{--}1290$  and  $1182\text{ cm}^{-1}$ ) and for the symmetric stretching ( $1190\text{--}1120$  and  $1029\text{ cm}^{-1}$ ). Such signals define the addition of sulphonic groups and the wide band at  $1182\text{ cm}^{-1}$  observed for the 100 %mol at 1 and 2 hours indicate that the higher amount of sulphuric acid the more sulphonation reactions are happening in the copolymers [10]. Proença [9] also observed such changes in the sulphonated styrene and Acosta [11] for the rising band at  $1005\text{ cm}^{-1}$  when sulphonating poly(styrene-butadiene) copolymers.

Thermogravimetric analysis was also carried out in order to evaluate thermal stability for non and sulphonated copolymers. Figure 3 shows the weight loss curves for the materials.

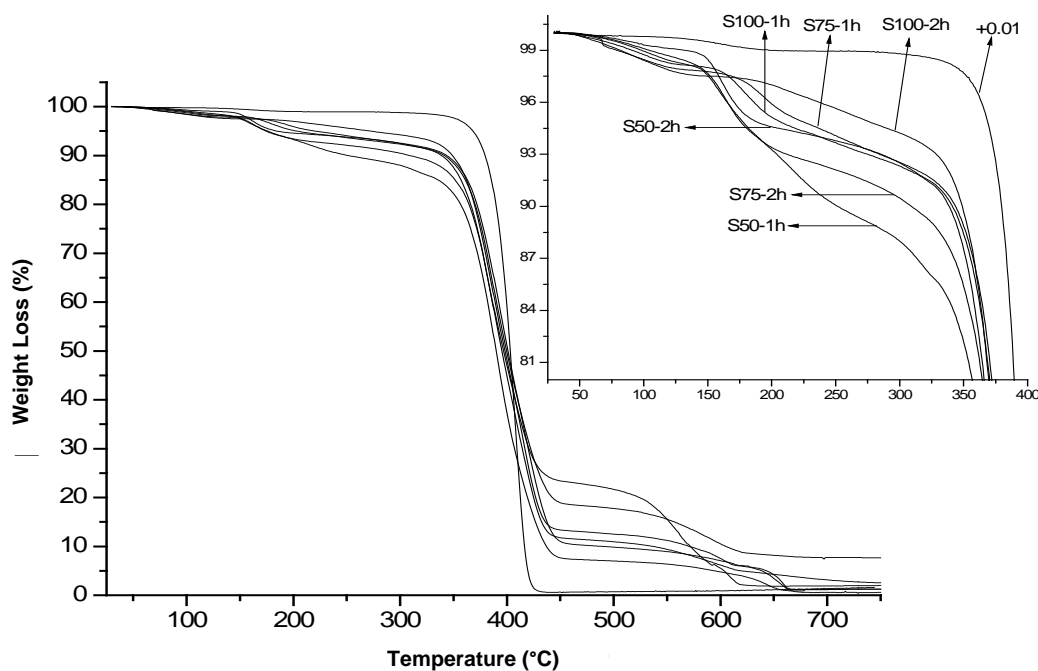


Figure 3. TGA thermograms for sulphonated copolymers

It is easy to note that non sulphonated material (+0.01) is the most thermally stable, showing basically one decomposition step at around  $350\text{ }^{\circ}\text{C}$  with no residues left. On the other hand, sulphonated materials decompose in several steps. The first step ( $50\text{--}140\text{ }^{\circ}\text{C}$ ), is basically associated with water loss, involved into the material due to the

hydrophilic characteristic induced by the sulphonic groups; it actually follows a tendency of more mass loss with higher sulphonating agent used to prepare them. A second step (150-350 °C) is associated to de-sulphonation reactions with a tendency to stabilize with higher level of sulphonation, as was reported by other authors [12, 13]. The third and main step is due to the copolymer backbone decomposition (350-450 °C). Finally, the fourth step is related to the level of residues left for each material, which is difficult to associate to a specific reaction, but in our case are showing fewer residues for lower level of sulphonation.

Dynamic Mechanical Analysis (DMA) was carried out to follow the viscoelastic property changes through sulphonation. Figure 4 shows the elastic modulus traces for the materials.

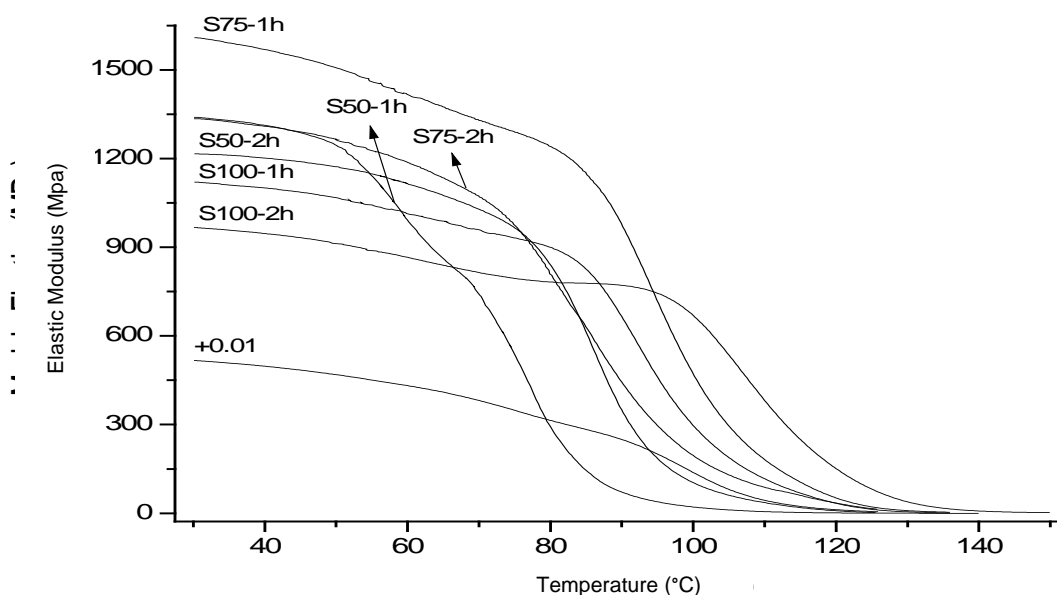


Figure 4. Elastic modulus ( $E'$ ) for non and sulphonated copolymers

The most important observation is that all sulphonated copolymers have higher elastic modulus values at room temperature than non sulphonated material. This is a consequence of some crosslinking reactions or strong interactions among sulphonic groups grafted to the main structure. There is also an important tendency clear to see, where the higher and longer sulphonation condition the lower the  $E'$  values at room temperature, which is related to the amount of water into the molecular structure; the more sulphonation means higher hydrophilicity and a more plasticized material. The latter behaves according to TGA first step weight loss due to water loss. Finally, if the main loss of the curve is considered as the vitreous transition ( $T_g$ ), the same high sulphonation means higher  $T_g$  values, which is also a consequence of the strong internal interactions reducing molecular mobility.

Figure 5 shows the viscous modulus for the same samples obtained during the same DMA evaluations. Same tendency is observed in  $T_g$  values, if the peak maxima are considered as the thermal transitions, having congruency

with  $E'$  results where more sulphonating agent and longer reaction times induce a more resistant material to suffer thermal transitions.

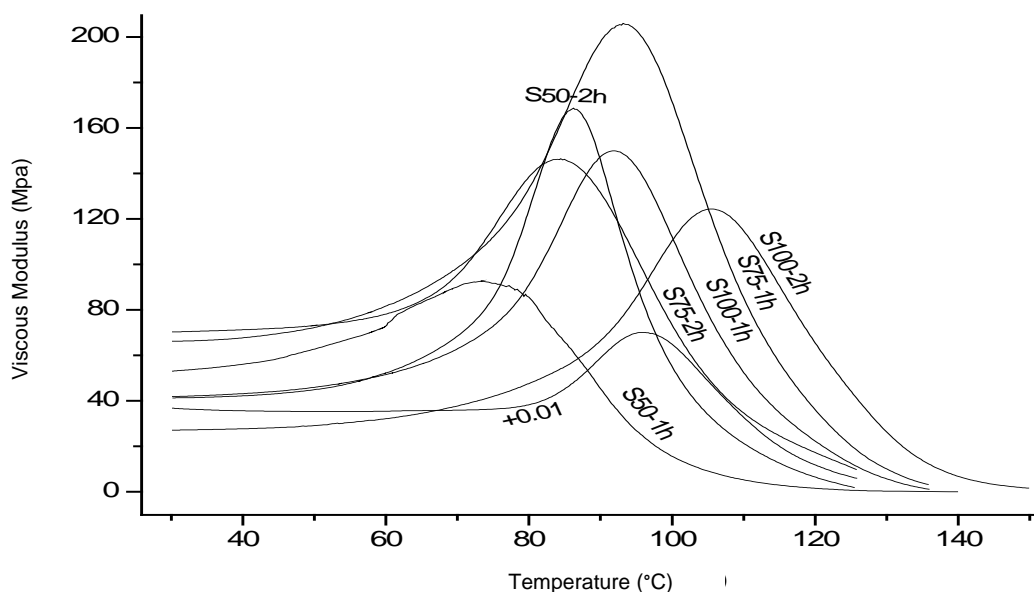


Figure 5. Viscous modulus ( $E''$ ) for non and sulphonated copolymers

Considering that water absorption in the materials play an important role, measurements were carried out to compare the copolymers through the sulphonation conditions. Figure 6 shows the results obtained.

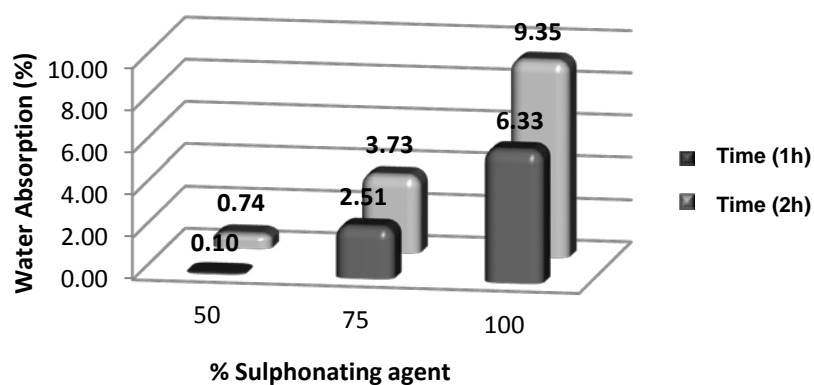
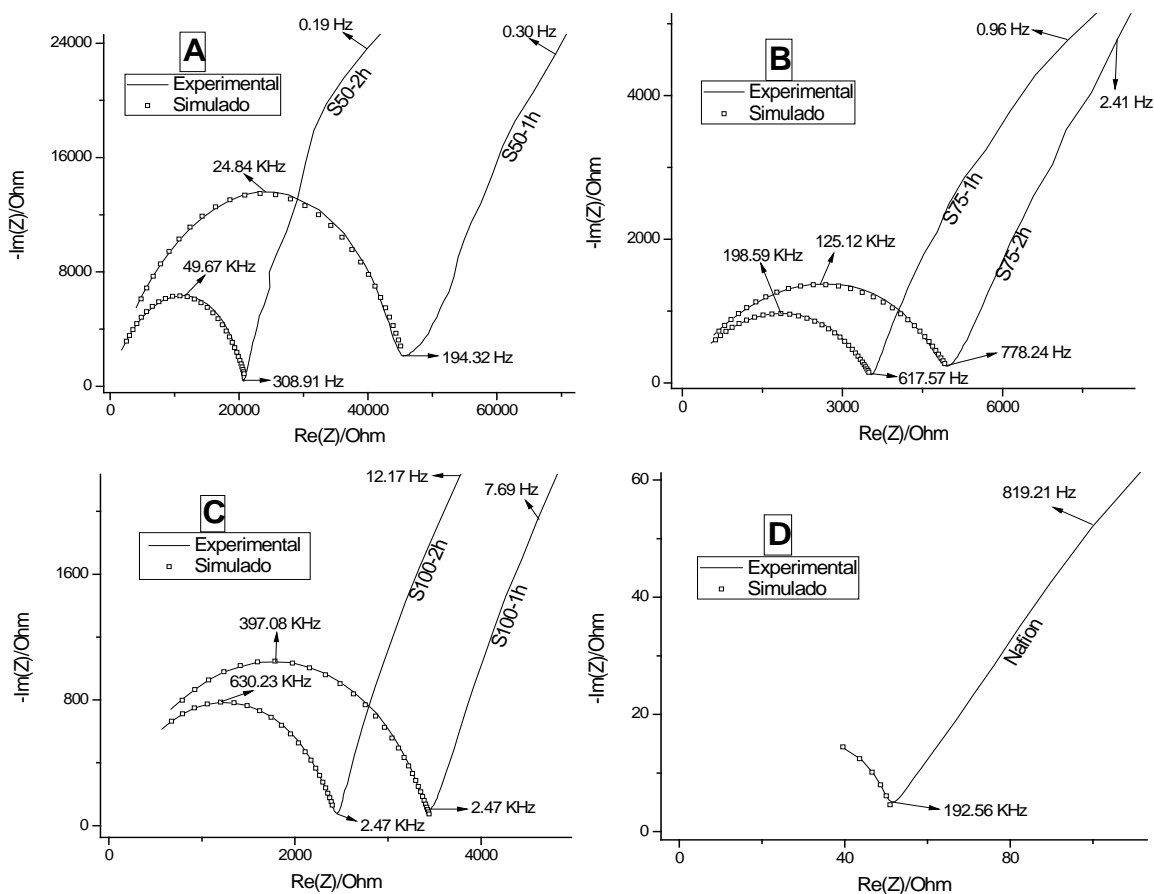


Figure 6. Water absorption for sulphonated samples

It is very easy to notice that for the higher amount of sulphonating agent and longer reaction time the absorption of water is enhanced, corroborating the previous results where a water intake was detected and used for discussions. According to sulphonation conditions, sulphonic groups graft into the main copolymer structure, enhancing hydrophilicity and changing their thermal and mechanical characteristics. Several authors have observed similar effect of sulphonic groups for polymer materials [14, 15].

The electrochemical behavior of sulphonated copolymers was evaluated by Electrochemical Impedance Spectroscopy (EIS) and compared with Nafion 117. The impedance spectra (Nyquist), simulated curves and the equivalent circuit are shown in Figure 7.





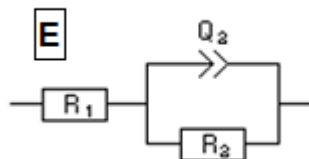


Figure 7. EIS spectra for sulphonated copolymers and equivalent circuit for adjusted curves (E)

The Nyquist impedance spectra involve the real ( $\text{Re}(Z)$ ) and imaginary ( $\text{Im}(Z)$ ) axes and their data is only adjusted or simulated in high frequency region (semi-circle) since lower frequencies describe diffusion and other phenomena out of our interest. From simulated curves several electrochemical parameters were obtained: ohmic resistance from the membrane ( $R_1$ ), constant phase element ( $Q_2$ ) and resistance to charge transfer ( $R_\infty$ ). Such parameters are useful to compare materials and from  $R_1$  the proton conductivity ( $\sigma$ , with S/cm units) can be calculated through the Ho equation [16]:

$$\sigma = \frac{Q_2}{R_1 \cdot A}$$

where “e” is membrane thickness and “A” area of transversal section. In our experiments the hole containing mercury is  $0.45 \text{ cm}^2$ . Figure 8 shows the proton conductivity obtained for sulphonated materials.

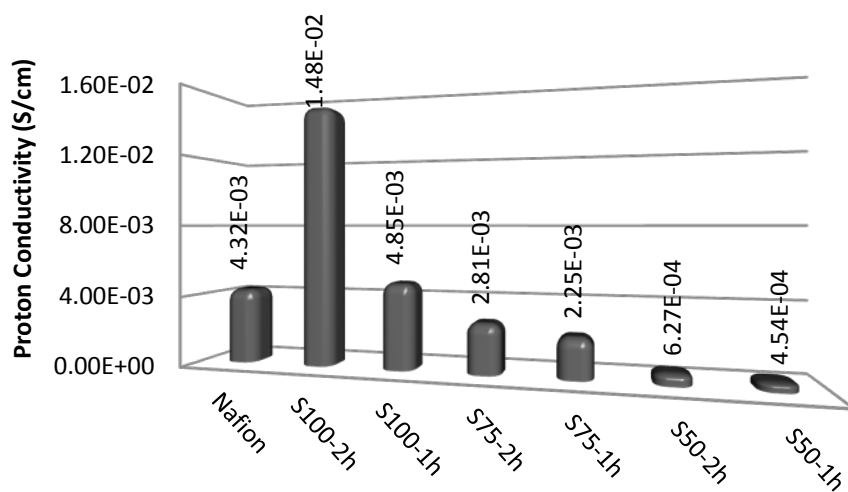


Figure 8. Proton conductivity ( $\sigma$ ) for sulphonated copolymers and Nafion 117.

A very clear tendency to enhanced proton conductivity values is seen for copolymers treated with higher amount of sulphonating agent and longer sulphonation time, noticing that copolymer with 100 % mol sulphonation, even during 1 hour, have higher values than Nafion. Such values are in direct proportion to ohmic resistance ( $R_1$ ), which in turn has the most influence to ohmic resistance of a fuel cell.

Proton conductivity values (ohmic resistance) have an important effect in the membrane polarization curves, which in turn are very useful to determine fuel cell performance. It is also directly related to absorbed water in the membrane, since proton conduction occurs by diffusion through the water inside hydrated clusters.

#### **4. Conclusions**

Evaluation of sulphonated copolymers of crosslinked poly(styrene-co-acrylic acid) indicated that presence of sulphonic groups which induce increment in  $T_g$  values, similar thermal stability and higher elastic modulus. The higher amount of sulphonating agent and longer times of sulphonation reaction reduce slightly such high elastic modulus as a consequence of higher water absorption but enhance proton conductivity. The most sulphonated membrane, by concentration of agent and longer reaction time (S100-2h), had a distinguished performance, since even with less ability to absorb water obtain higher level of proton conductivity when comparing with Nafion.

#### **5. Acknowledgments**

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