International Journal of Applied Engineering Research
ISSN 0973-4562 Volume 10, Number 6 (2015) pp. 15905-15913

http://www.ripublication.com

Synthesis Of A Proton Exchange Membrane Obtained From Sebs Copolymer For Application In A Fuel Cell

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ABSTRACT

In this work, a proton exchange membrane was obtained using SEBS copolymer, for application in a fuel cell. Furthermore, the SEBS copolymer was sulfonated to modify the physicochemical properties. The physicochemical properties were evaluated considering the comparation with the unmodified membrane. The membrane with sulfonated exhibited low values of water uptake (5,94%) and capacity of ion exchange (0.151meq/g). By infrared spectroscopy analysis (FTIR) was found in the sulfonated membranes peaks 873-840 cm^{-1} being observed the addition of sulfonic acid groups in the membrane due to the sulfonation. Furthermore, the proton conductivity is $1.16x10^{-7}$ S/cm at 60 ^oC, which is a similar value found in other investigations. These results demonstrate the excellent potential of prepared membrane for use in fuel cells.

Keywords: Membrane, SEBS, Proton exchange, Sulfonation, Fuel cells

1. INTRODUCTION

The current model of energy consumption, it's based on the burning of fossil fuels like oil, coal and natural gas, is unsustainable, for one basic reason: the deposits of these fuels are running out, its extraction has caused an imbalance causing severe environmental impact on the planet. The increase in emissions of greenhouse gases generated from combustion, have caused an increase in global temperatures with serious consequences [1]. This problem facing humanity into a global energy crisis, because it must seek alternative sources of energy before fossil fuels are exhausted and a socioeconomic problem arises on a larger scale. There are some alternative energy to replace the use of fossil fuels, generating greater economic and environmental impact, as in the case of fuel cells, which is defined as a device that converts the chemical energy of the reaction between hydrogen (H_2) and oxygen (O_2) into electricity and heat, the product of this reaction is water (H_2O), among which are the type of proton exchange membrane [2].

Research as developed by [3] have been conducted proton exchange membranes from copolymers such as Vinyl Acetate-Acrylic Ester and Styrene-Acrylic Ester, get results in mechanical properties due to the sulfonation, generating a high potential for use in fuel cells. The development of this proposal permits the study of membrane prepared using SEBS copolymer modified by sulfonation for evaluation of its mechanical and physicochemical properties in fuel cell applications. The results obtained were compared with those observed in the polymeric membrane Nafion, which is the most used, but has a low performance at high temperatures with high costs.

2. Experimental Procedures

2.1. *Materials*

The materials used in the experiment were: SEBS, distributed by Parabor Colombia (Bogotá), styrene, by the store "Resinas y Pinturas" (Cartagena), Sulfuric acid, acetic anhydride, metanol.

2.2. Membrane Synthesis

A solution of the copolymer 10 g of the SEBS were taken in a beaker containing 100 ml of the solvent styrene, heating the solution at a temperature of 200 ° C and agitating for the time necessary to achieve homogeneity. Then, it was carried out the sulfonation process using a sulfonating agent [4] mixed with copolymer solution in relation 1:1.

This solution was placed in agitation at room temperature for 4 hours, the solution was dismounted and the reaction is stopped with 50 ml of methanol until obtaining a precipitate of copolymer, and then filtered and drying in an extractor chamber for 15 minutes to obtain a better drying [5].

2.3. Membrane characterization

The *Water* uptake is defined as the percentage of adsorbed water in the wet membrane. For this test the membrane was immersed for 3 days in a container with distilled water; then extracted and excess water was removed with a filter paper, the wet weight of the sample was calculated (W_h). Immediately the membrane was dried at 75 ° C for a time of 2 h was weighed, to determine the weight of the dried sample (W_s). The percentage of water retention was calculated by the following expression [6].

$$\%\ Water\ Uptake = \left(\frac{W_h - W_s}{W_s}\right) * 100 \tag{1}$$

The ion exchange capacity is defined as the number of moles of SO_3 per gram of polymer fixed, indicating the capacity of the ion transfer membrane [7]. The percentage of water uptake is calculated by the following equation [8]:

$$Ion\ Exchange\ Capacity\ (IEC) = \left(\frac{V_{NaOH} * [NaOH]}{m}\right) \tag{2}$$

Where: V_{NaOH} is the volume of NaOH used in the titration, $[NaOH]$ is the concentration of Na^+ and *m* is the mass of dry membrane.

The proton exchange membranes are characterized by a definable ion exchange capacity as the number of millimoles of H^+ per unit mass of dry membrane. This process is carried out by immersion in a solution of HCl for 24 hours. Then, the membrane is immersed in 50 ml of 1M NaCl for another 24 hours to produce the ion exchange between protons in the membrane and sodium ions. The solution was titrated with NaOH to the equivalence point [9].

The mechanical properties were determined resistance to stress, Young's modulus and elongation. For this purpose a tensile test was carried out, using the universal machine Instron 4411 Quality Lab.

Infrared spectroscopy (FTIR) was carried out by the method of the Fourier transform (FTIR) to determine the interaction of sulfonic acid groups attached to the membrane through sulfonation using the spectrophotometer Nicolet 6700 [10].

2.4. Determination of proton conductivity

The proton conductivity was carried out using electrochemical impedance spectroscopy technique. A method used in corrosion studies which is based on an alternating current signal that is applied to an electrode and determining the corresponding response [9]

To calculate the proton conductivity was used the following equation:

$$\sigma = \frac{d}{RS} \qquad (3)$$

where σ is conductivity (S/cm-1), *d* is the sample thickness (cm), *S* is area of the sample in contact with the electrodes (cm^2) and *R* is the resistance to the sample (Ω). Proton conductivity test was carried out using electrochemical impedance spectroscopy equipment (HIOKY 3532-50). For the test were used samples of the sulfonated membranes with dimensions of 0.5 x 0.5 cm.

3. Results and Discussion

3.1. Membrane Synthesis

3.2. Water Uptake

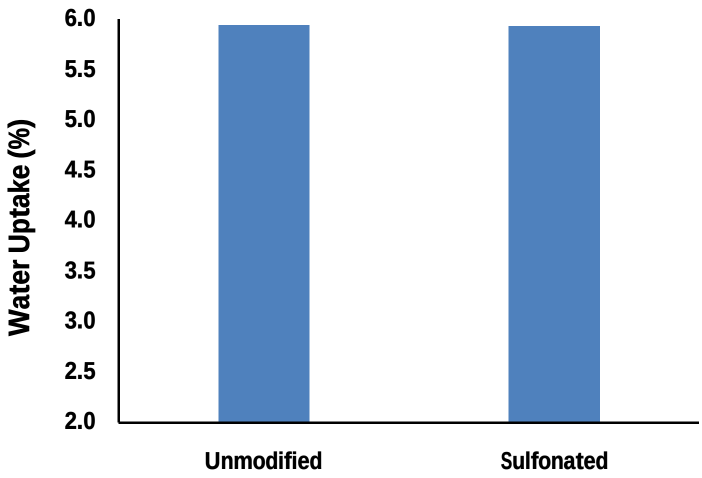

Figure 1. Water uptake of prepared membranes

Figure 1 shows the effect of sulfonation on the water uptake of the membranes. Water uptake was no affected by sulfonation reaction. In the sulfonation reaction is bonding chemically the sulfonic group ($-SO_3H^-$) to a carbon atom of the SEBS copolymer molecule [11]. However, sulfonated membranes presented low percentage of water uptake, together with the membrane unmodified. So it can be said that the cause of water absorption in this copolymer is given by the addition of charge as observed in [12]. On the other hand, Fernandez [13] SEBS dissolved in THF and this copolymer presented a water uptake of 74.3%, while in this work, the copolymer was dissolved in styrene, which affected the inclusion of the sulfonic group to the polymer chain.

3.2. Ion Exchange Capacity (IEC)

The sulfonated membrane has exchange capacity lower than the unmodified membrane. Generally, the ion exchange capacity should increase with the sulfonation [6]; however, sulfonation reaction with SEBS was affected by crosslinking between styrene and sulfonic group as observed in Figure 2.

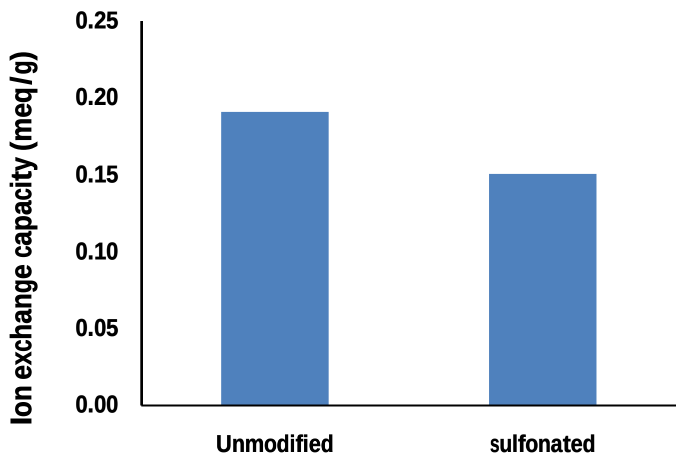

Figure 2. Ion Exchange Capacity of prepared membranes

3.3. Mechanical Properties

Table 1 indicates mechanical properties of tensile strength, elongation and Young's modulus. The sulfonated membrane has a low resistance to stress, because the use of high temperature in the sulfonation process, to initiates the polymerization of styrene of low molecular weight which causes poor mechanical properties of the sulfonated membranes.

The tensile strength of the membranes prepared is lower compared to the Nafion ® membrane NRE 211-10 (8.3 MPa). However, in other investigations have found membranes with values of maximum tension lower than Nafion membrane values which have been used in fuel cell [14, 15].

Table 1. Mechanical Properties

Muestra	tensile strength (MPa)	elongation (%)	Young's modulus (Mpa)
Unmodified	7,7	106,86	1123,9
Sulfonated	2,6	4,06	460,8

3.5. FTIR spectroscopy

Infrared spectroscopy is extremely useful for the qualitative determination of organic compounds and to deduce molecular structures from their functional groups both organic and inorganic compounds [16].

Figure 3 shows the FTIR spectrum for each of the membranes in an absorption band located between 600 and 3500 cm^{-1}. Spectrum for each of the sample of SEBS has peaks ranging from 696 to 757cm^{-1}, representing the presence and the deformation corresponding to the vibration of aromatic ring out of plane, of C-H bond of the SEBS. The band 1600 cm^{-1} corresponds to the stretching vibration of aromatic rings. The sulfonated membrane has band ranging from 873-840 cm^{-1} indicating the existence of the phenyl group distributed by the sulfonation of aromatic rings [13].

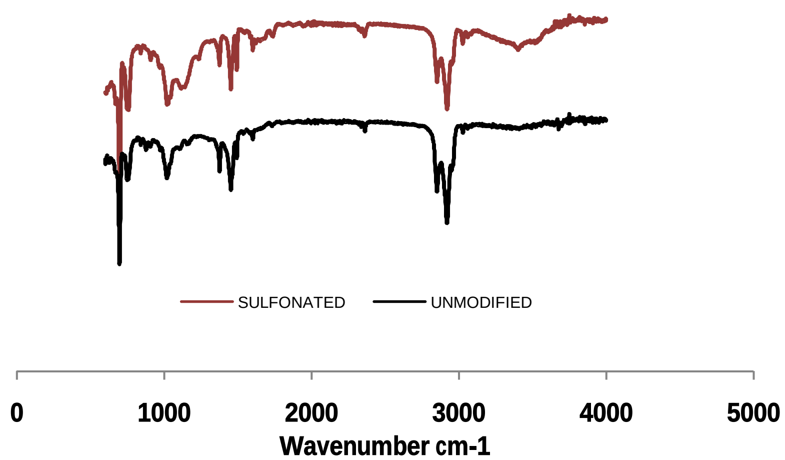

Figure 3. FTIR spectra of prepared membranes

3.6. Proton Conductivity

Membrane conductivity depends on the amount of water uptake and Ion Exchange Capacity, which involves the dissociation of the protons of the groups HSO_3^- and their transport across the water, and groups SO_3 [13] fixed in membrane.

The impedance test was performed at a constant temperature of 60 °C, due to the operating temperature of the fuel cell type polymer membrane is 80 °C, which is imposed by the membrane material currently used, Nafión® of Dupont [17]. Figure 4 shows impedance spectra Z Using the representation of Nyquist in function of Z` and Z", where Z` is the real part and Z`` is the imaginary part of Z [18].

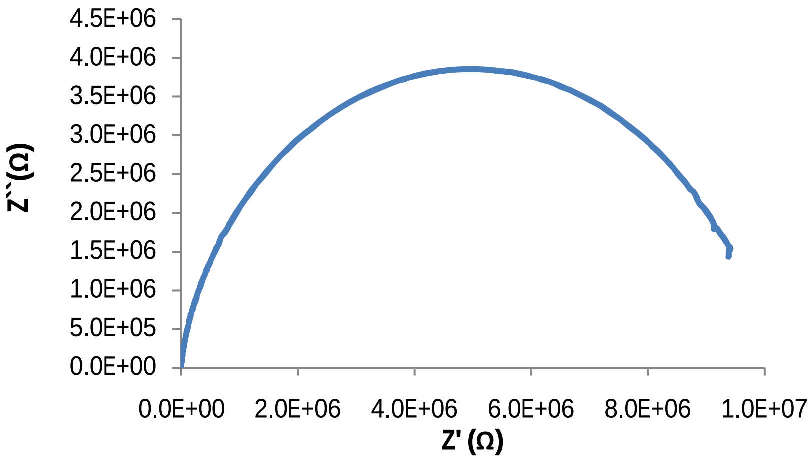

Figure 4. Proton conductivity prepared membranes

The proton conductivity of the membrane is calculated by the equation 3 where the membrane has thickness of 0.272 cm, an area of 0.25 cm, and a *R* obtained in the Nyquist diagram of $9{,}38x10^6$ Ω obtaining a proton conductivity of $1.16x10^{-7}$ Scm^{-1} at 60 °C. This proton conductivity is lower than proton conductivity ($6.6x10^{-2}$ Scm^{-1}) of Nafion 117 membrane at 100 °C and 100% relative humidity [13]; although, the Nafion 117 was operated at a higher temperature than prepared membrane in this investigation, favoring high values. Generally, conductivity measurements increase with increasing temperature and the amount of HSO_3^- groups [19].

4. Conclusions

Membranes were prepared using SEBS copolymer dissolved in styrene. This copolymer was modified by sulfonation, which was reflected in the infrared spectroscopy spectra, since the peaks were detected equivalent to the sulfonic groups; however, the values of water uptake and ion exchange capacity are relatively low compared to the membrane without modification. High temperature was necessary to dissolve the copolymer, and this could lead to instability in the membrane. which was evident in the low mechanical properties. However, the proton conductivity value is similar to prepared membranes in other investigations, indicating good potential for application in fuel cell.

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