Effect of Sulfonation of SEBS Copolymer on the physicochemical properties of Proton Exchange Membrane

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Abstract— In this work, proton exchange membranes were prepared using SEBS copolymer, for application in a fuel cell. The SEBS copolymer was modified with the addition of a TiO_2 load to prepare sulfonated and unmodified membranes. The sulfonated–loaded membrane exhibited higher values of water absorption (16%) and ion exchange capacity (1.13 meq/g) due to a significant increase in porosity, which increased the surface area and facilitated the ion exchange phenomenon by the formation of complexes between the sulfuric acid and TiO_2; however, the low stability of the membrane prevented the applications of impedance and mechanical testing. The membranes were analyzed by Fourier transform infrared spectroscopy (FTIR), to check the modification of the SEBS; however, there were no bands that will determine the presence of TiO_2 in the copolymer.

Keyword- Membrane, Proton exchange, sulfonation, fuel cell.

I. INTRODUCTION

The development and advancement of technologies can not be stopped by the projected depletion of natural resources, for this is required the search for new processes to supply the energy needs, which can not be supplied by fossil fuels in the future. Renewable energies have been visualized as a promising option of catering due to allow the use of local resources giving energy to lower economic and environmental costs, compared to the conventional. These are resources capable of renewed indefinitely, among which are highlighted solar, thermal, geothermal, hydro, biogas, wind and from hydrogen like fuel cells.

The Fuel cells converts chemical energy of hydrogen into electrical energy, as result of this conversion only water and heat are produced as waste [1]. The fuel cells have advantages like being environmentalist, having less moving parts and not requiring maintenance continuously. Fuel cells are one of the most promising technologies for delivering clean and efficient power to automotive and residential applications. With increased urgency in reducing pollution and greenhouse gas emissions, a resurgence of interest in fuel cells has occurred [2].

The developed in this paper allows the study of SEBS copolymer membrane modified with sulfonation and/or addition of TiO_2 for the evaluation of its mechanical and physicochemical properties for fuel cell applications. The results obtained were compared with those observed in the most used polymeric membrane Nafion, but has a low performance at high temperatures with high costs, reasons that have impeded their marketing.

II. MATERIALS AND METHODS

A. *Materials and instruments*

The materials used in the experiment were: SEBS Fortiprene, distributed by Parabor Colombia (Bogotá), styrene, by the store "resinas y pinturas" (Cartagena), Titanium Dioxide, by drugstore Juliao (Cartagena), Sulfuric acid, acetic anhydride, methanol.

B. *Membrane Synthesis*

To the copolymer solution, 10 g of the pure SEBS resin were taken in a beaker with 100 ml of solvent styrene, heating the solution to a temperature of 200°C and stirring for the time required to obtain homogeneity.

C. *Adittion of TiO_2 load*

One of the solutions developed in the previous experiment, is subjected to the addition of a solution of commercial TiO_2 (titanium dioxide) in 0.1 M NaOH very low concentration (don't affect the polymer properties) in order to improve the conductivity of the membrane. Preparation of 0.1 M solution of TiO_2 was made from a solution of 100 ml 1M NaOH with 0.8 grams of the charge then dissolved in the solution of the polymer with the solvent. For the preparation of the hybrid membrane (sulfonated-loaded) takes solution of SEBS explained in [3].

D. *Membrane Characterization*

1) Water Uptake: This property is defined as the percentage of adsorbed water in the wet membrane. For this test the membranes were 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. Immediately the membrane was dried at 75 ° C for a time of 2 h and then was weighed [4]. Water uptake was defined with the following equation:

$$Water\ Uptake\ (\%) = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) * 100 \qquad (1)$$

where W_{wet} and W_{dry} are the weights of wetted and dried membranes, respectively [5].

*2) Ion Exchange Capacity (IEC):*The ion exchange capacity is defined as the number of moles of SO3 per gram of polymer fixed, indicating the capacity of the ion transfer membrane [6]. The ion exchange capacity (IEC) of SEBS were determined by the titration method [7] The samples were immersed in a solution of HCl for 24 hours. Later immersed in 50 ml of 1M NaCl for another 24 hours to produce the ion exchange between protons between the membrane and sodium ions. The solution was titrated with NaOH to the equivalence point [4].

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

where V_{NaOH} is the volume (L) of NaOH used in the titration, [NaOH] is the concentration of Na^+ and m is the mass (g) of dry membrane [8].

3) FTIR Spectroscopy: Infrared spectroscopy was held by the method of the Fourier transform (FTIR). To test the interaction of sulfonic acid groups bound to the membrane through sulfonation and the presence of load TiO_2, using the spectrophotometer Nicolet 6700 [9].

III. RESULTS AND DISCUSSION

E. *Effects of the addition of TiO_2*

The addition of TiO_2 presented a swelling reaction in the membrane, due to the TiO_2 is not soluble in styrene, which was used as solvent of copolymer, generating a decrease in the diameter of the membranes, which can be observed in the figure 1a; while the sulfonated-loaded membrane was swollen and broken as shown in Figure 1b, which is associated with the addition of heat before and after the sulfonation.

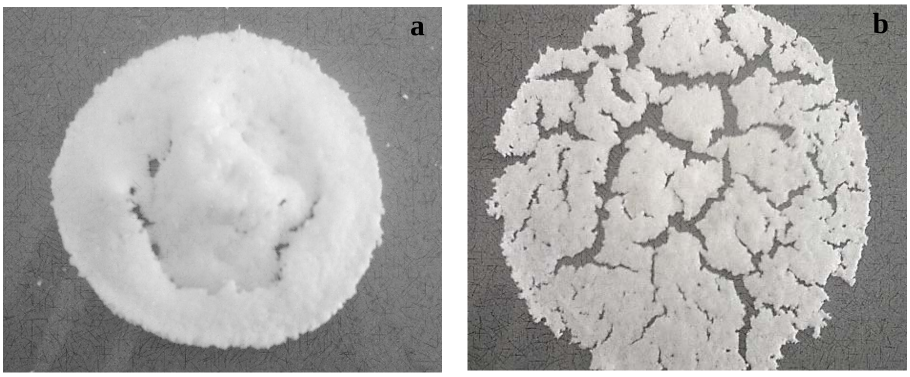

Fig 1. Membrane prepared. a) Loaded membrane b) sulfonated-loaded membrane.

F. *Water uptake*

Figure 2 shows water uptake of loaded and sulfonated–loaded membranes. The sulfonated-loaded membrane presents a water uptake percentage of 16%, while the loaded membrane has a value of 7.8%.

Water Uptake increased considerably with the sulfonation, due to the micropores formation in the membrane, by the effect of the heat used to dissolve the membrane after sulfonation and adding titanium dioxide. The heat causes an increase in the opening of the micro-pores and the formation of groups of hydrated, leading to an increase water uptake in the membranes [10, 11]. By other side, the sulfonation causes addition of sulfonic groups to the copolymer, that form the ionic cluster which are of polar nature and increasing the percentage of hydrophilicity of the copolymer, giving rise to increase of water uptake.

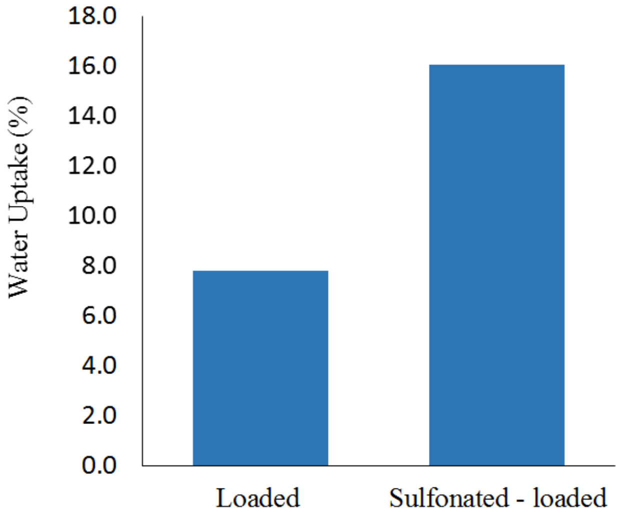

Fig 2. Water Uptake of prepared membranes.

G. *Ion Exchange capacity*

Figure 3 shows the ion exchange capacity for the sulfonated–loaded and loaded membranes. It is observed a large difference between the two types of membranes. The value of loaded membrane decreases with respect to the addition of sulfonic acid groups on the copolymer. Ion exchange capacity (IEC) is an important parameter of membrane related to its conductivity, because it links to the density of ionizable functional group in the membrane [12], in this study the IEC is related with the inclusion of the sulfonic groups in the membrane by the sulfonation reaction.

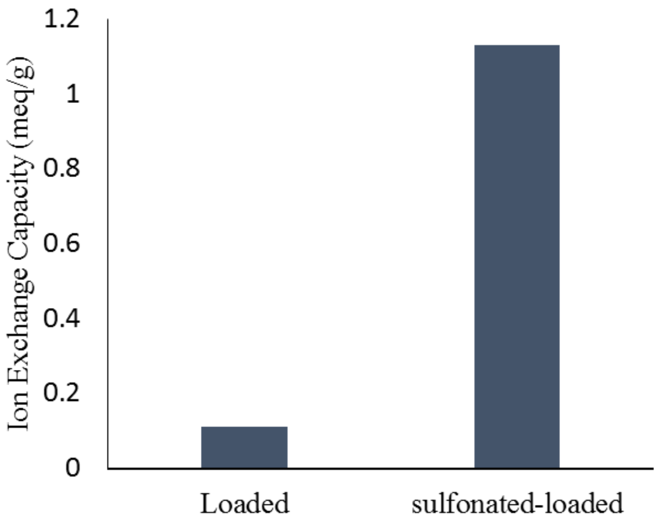

Fig 3. Ion Exchange Capacity of prepared membranes.

The loaded-sulfonated membrane presents a high value of ionic exchange capacity. The presence of the sulfonics groups in the copolymer increase the number of available sites for proton conduction in the polymer network [13]. Moreover, the ion exchange capacity is related to the water uptake, these effects were provided by the sulfonation, so there is a concordance between IEC and the water uptake in this study. However, in other research [14] the SEBS copolymer shows values for IEC of 1.62 meq/g, which is a value greater than the one presented in this study for the sulfonated-loaded membrane, due to agglomerations that formed by adding the loaded.

A. *FTIR spectra of prepared membrane*

Infrared spectroscopy was performed to analyze the bands of the sulfonic groups and the addition of the load to copolymer. Figure 4 shows the values thrown by the test of FTIR for the loaded and sulfonated–loaded membranes. The loaded and sulfonated-loaded membrane shown the same peaks, however in the loaded membrane these are more pronounced, and also presents a peak at 2359 cm^{-1} a frequency characteristic of copolymer SEBS is reflected in both samples present in 696 cm^{-1} [15].

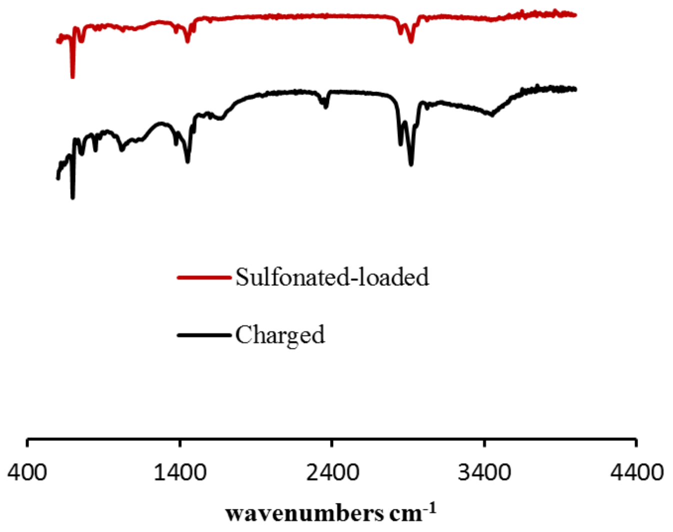

Fig 4. Ion Exchange Capacity of prepared membranes.

The spectrum for each of the samples presents a band ranging from 696-762 cm^{-1} which represents the presence and deformation of the aromatic ring which corresponds to vibrations out of the plane of the bond CH of the SEBS [3]. The correspondence of bands for Ti-O-Ti have values of 550 cm^{-1} [16], however the samples have not similar values to the detection limits of the FTIR, so it was confirmed the weakness of adhesion of the load at the membranes, since observed that smaller values at the peaks of each of the membranes are 600 cm^{-1}.

IV. CONCLUSION

In the present investigation, photo-electrodes of titanium dioxide supported on aluminum, glass and graphite were prepared. It was established that any of these materials has an effect that would alter the crystal structure of titanium dioxide, and consequently the photonics exhibition; however, the surface characteristics of graphite do not allow adequate adhesion of the TiO_2 film, which is a limiting factor for the occurrence of the photo-electrochemical process. Aluminum substrate has the best performance in the process of photo-electrochemical water splitting by its capacity of electrical conduction, which favored the movement of photocurrent. Therefore, the aluminum provides stability during thermal treatments in the preparation of the photoelectrode. The solvent employed favored the adhesion of the films; however this promotes agglomeration of the particles.

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