Effect of the Sulfonation in a Proton Exchange Membrane from n-Butyl Acrylate/Styrene Modified with Fe$_2$O$_3$ for Fuel Cells

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Abstract

Synthesis of proton exchange membranes was carried out from n-butyl acrylate/styrene modified by sulfonation and loading of ferric oxide to evaluate its use in fuel cells. Its physicochemical and mechanical properties were characterized. The results showed that the sulfonation improved the water uptake of the membrane due to the hydrophilic character contributed by the sulfonic groups, also enhancing the ion exchange capacity. With the FTIR analysis the modification of the copolymer was evidenced. Despite the low mechanical properties obtained by the loaded-sulfonated membrane, this presented the best characteristics for the transport of protons, due to the hygroscopic properties added by the ferric oxide, allowing a better interaction with the polymeric matrix, and with the joint action of the sulfonic groups, it was further improved, evidenced in the proton conductivity result, so this membrane presents high potential for its use as an electrolyte in fuel cells.

Keywords: n-Butyl Acrylate/Styrene, Proton Exchange Membrane, Sulfonation, Ferric Oxide, Fuel Cells.

INTRODUCTION

The great demand for energy that exists today, climate change and the high degree of pollution caused by the burning of fossil fuels have boosted interest of developing alternatives that make it possible to obtain electricity in a cleaner way [1]. Fuel cells emerge as an option to mitigate this problem, converting chemical energy directly into electrical energy, with high efficiency and zero emissions [2]. Within this group of fuel cells are the proton exchange membrane fuel cell (PEMFC) type, whose fuel is hydrogen which has an energy power per unit mass almost three times higher than gasoline [3]. The most relevant polymeric membranes today are the Nafión® manufactured by DuPont, these have good thermal stability, chemical and high proton conductivity, but are expensive, can have problems of permeability and its conductivity tends to decrease at temperatures above 80 °C and low hydration [4], so it is necessary to study new polymeric materials that allow to compete with the membranes that are currently marketed. It has been found that the combination of polymeric materials can improve the properties of polymers separately [5, 6], similarly, applying sulfonation procedures and addition of inorganic filler also tends to improve its performance [7, 8]. In the present research project, proton exchange membranes were synthesized from the n-butyl acrylate/styrene copolymer modified with sulfonation and addition of ferric oxide to evaluate their physicochemical and mechanical properties, and to determine their possible application as an electrolyte in fuel cells.

EXPERIMENTAL PROCEDURES

Materials

Copolymer of n-butyl acrylate/styrene, ferric oxide, sodium hydroxide, distilled water, acetic anhydride, sulfuric acid, methanol, hydrochloric acid and sodium chloride were used for the synthesis and characterization of the polymeric membranes.

Membrane synthesis

Unmodified, sulfonated and loaded-sulfonated membranes were prepared. The unmodified membrane was obtained by dissolving 20 g of the copolymer in 20 ml of distilled water, with magnetic stirring at 250 rpm in a 1000 ml flat bottomed flask until a homogeneous solution was reached, which was divided into two aliquots of 20 ml, one of these was dosed in two Petri dishes, pouring 10 ml in each. For the sulfonated membrane, 20 g of the copolymer was dissolved in 10 ml of distilled water under the same operating conditions, in parallel, 10.8 ml of acetic anhydride was dissolved in 100 ml of distilled water in a beacker, which was previously located in a bath of ice, 6.7 ml of sulfuric acid was added and left in reaction for 10 minutes to obtain the sulfonating agent [7]. The sulfonating agent was added dropwise to the solution of the previously prepared polymer and left under constant stirring at 250 rpm and a temperature of approximately 80 °C for 3 hours, after this time the heating and stirring were deactivated to stop the reaction when adding methanol, a solution of approximately 150 ml was obtained, of which 70 ml were taken and divided into two aliquots of 35 ml to be dosed in Petri dishes. The loaded-sulfonated membrane was obtained by preparing 100 ml of an aqueous solution of 10% NaOH to which was added 0.8 g of Fe$_2$O$_3$ corresponding to a load of 4% (% w/w) and left with magnetic stirring at 250 rpm for 4 hours, after this time 50 ml of this solution was taken and mixed with the remaining 70 ml of the sulfonated membrane preparation by magnetic stirring at 250 rpm until a homogeneous mixture of purple color was observed, the final solution was approximately 120 ml that were dosed in Petri dishes.

Membrane Characterization

The water uptake of the membrane was determined when calculating its weight variation, before (W_d) and after (W_w) of immersing samples in distilled water for 24 hours [9]. The ion exchange capacity was obtained by applying the titration method, initially samples of the membrane were submerged in a solution of 1 M HCl for 24 hours, then relocated in a solution of 1 M NaCl for 24 hours more to produce the exchange between the ions of sodium and the membrane, and finally the point of equivalence is determined with NaOH [5]. The mechanical properties such as tensile strength, elongation to rupture and Young's modulus were characterized through an EZ-S Universal Shimadzu texturometer. The conductivity of the membrane was determined by means of the electrochemical impedance spectroscopy technique, using the Solatron 1260A Impedance Analyzer, the sample analyzed had a diameter of 0.985 cm and a thickness of 0.035 cm, a voltage of 100 mV was applied in a range of 50 Hz - 5 MHz at a temperature between 50 °C and 80 °C since this is the temperature range in which the PEMFCs traditionally operate [2]. An infrared spectroscopy analysis was applied to determine the modifications caused by sulfonation and addition of load by means of a Nicolet 6700 Fourier Transform Spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the three types of membranes synthesized, each characterized by water uptake, ion exchange capacity, mechanical tests, conductivity and FTIR analysis.
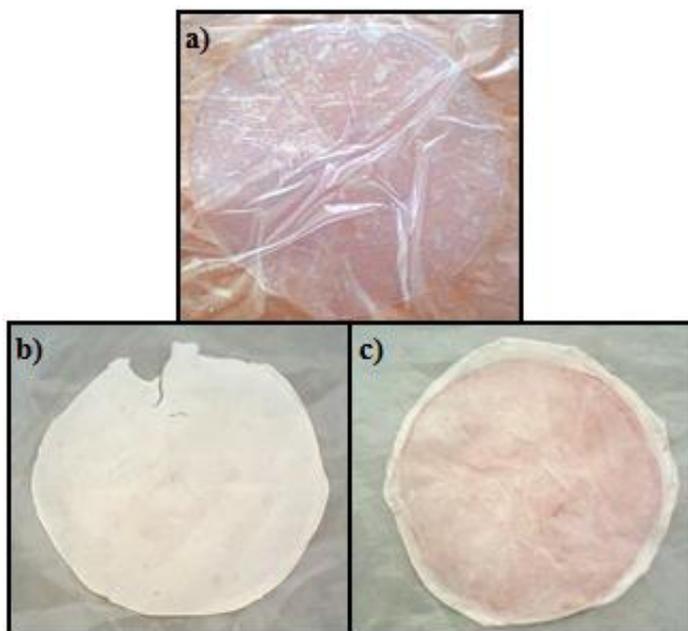

Figure 1. Prepared membranes: a) Unmodified (UM), b) Sulfonated (S), c) Loaded 4% - Sulfonated (L 4% - S)

Water uptake

Figure 2 shows that the unmodified membrane has a low water uptake, caused by the high hydrophobicity of the copolymers associated with the n-butyl acrylate blocks [10] and styrene [6].

The water uptake was raised to 56.02% for the sulfonated membrane, this increase is due to the hydrophilic character contributed by sulfonic groups (SO_3H^-), which improve this property through the formation of hydrogen bonds with water molecules [11].
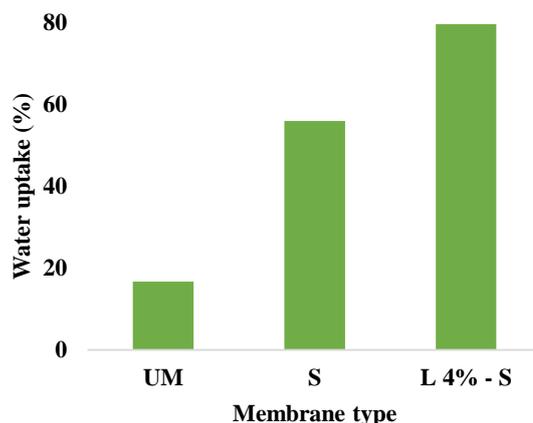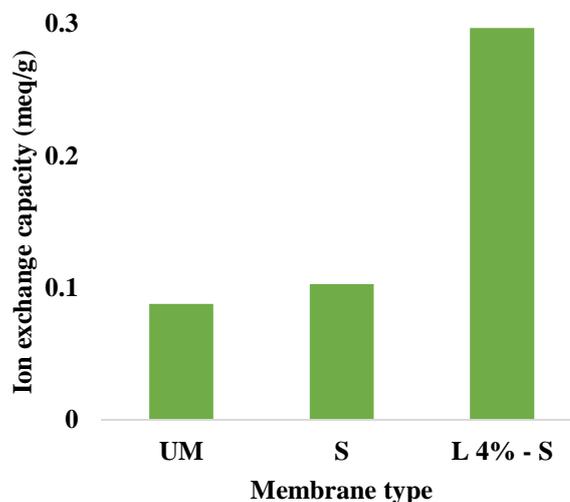

Figure 2. Water uptake for each membrane.

In the loaded-sulfonated membrane the value of 79.64% is reached, caused by the combined effect of the sulfonic groups and the inorganic load, due to the hygroscopic properties contributed by the ferric oxide, allowing the highest water retention [12, 13]. This type of membrane far exceeds the water absorption values present in Nafion commercial membranes 115 and 117, being 26% [14] and 18% [15], respectively.

Ion exchange capacity

Figure 3 shows that the effect of sulfonation was favorable by increasing the ion exchange capacity of the unmodified membrane by 17.21%, because the added sulfonic groups provide new available sites for the conduction of protons inside the membrane [16].

Figure 3. Ionic exchange capacity for each membrane.

The incorporation of inorganic additives to sulfonated copolymers can improve the thermal, mechanical, chemical, and electrochemical properties [8], so by increasing the water uptake in the loaded-sulfonated membrane, the highest ion exchange capacity (0.296 meq/g) was obtained because water provides the means for the transfer of protons by means of the vehicle mechanism where protons diffusing together with water by forming hydronium ions, and the Grotthuss mechanism where proton hopping from one proton carrier site to a neighboring one [17].

Mechanical test

Table 1 shows that the loaded-sulfonated membrane had the lowest levels of mechanical properties caused by its high degree of water uptake, because the water uptake increases the size of the pores and the membrane matrix experiences some stress [18], also the absorbed water acts as a plasticizer or solvent for the membrane, and therefore results in the deterioration of the mechanical strength [19].

Table 1. Mechanical test for each membrane.

Membrane type	UM	S	L 4% - S
Breaking strain (Mpa)	1,65	1,92	1,3
Elongation to rupture (%)	1978,16	1237,27	1211,95
Young's modulus (MPa)	$13,3 \times 10^{-3}$	6×10^{-3}	$4,8 \times 10^{-3}$

The sulfonated membrane reached the highest value of breaking strain (1.92 MPa) because the sulfonic groups enhanced the rigidity between the bonds of the polymer chains [7], but at the same time they affected its response to elongation, evidenced by the decrease in this property, while the unmodified membrane presented the greater Young's modulus associated with the good elastomeric characteristics of the copolymer [20].

Proton conductivity

The electrochemical impedance analysis was performed on the loaded-sulfonated membrane since it presented the best ion exchange characteristics. In Figure 4 the impedance spectra Z is observed through the Nyquist diagram in function of Z' and Z'', where Z' is the real part and Z'' is the imaginary part of Z [21].
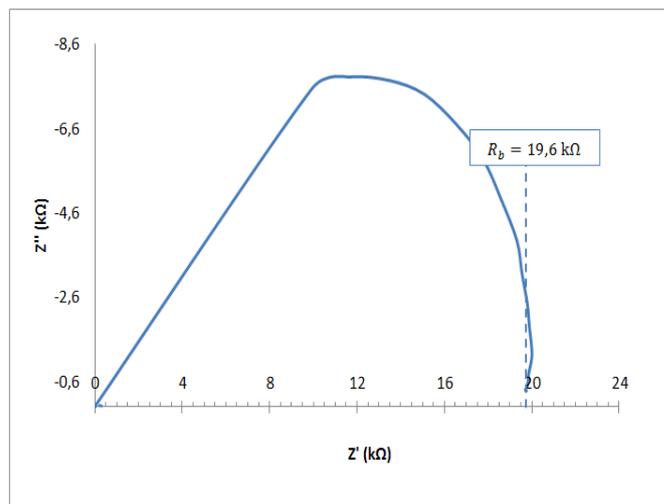
Figure 4. Nyquist diagram for the loaded-sulfonated membrane.

Taking into account the area of the membrane in contact with the electrodes, as well as its thickness, diameter and resistance R_b (19.6 kΩ) taken from the Nyquist diagram, the value of 1.913×10^{-3} S cm^{-1} was obtained as proton conductivity for the loaded-sulfonated membrane [22]. This protonic conductivity value is attributed to the fact that the electrochemical impedance characterization was carried out with an initial water content of 79.64% obtained during the water absorption test, however, the equipment operated without a hydration system, which did not allow constant humidification of the sample, so that the performance could deteriorate due to the decrease in water in the membrane, thus increasing its ohmic resistance [23], since the degree of hydration is directly related to the protonic conductivity because water allows transport mechanisms to occur [24]. Although the proton conductivity obtained for this membrane is less than the Nafion 115 of 8.13×10^{-3} S cm^{-1} [14] and Nafion 117 of 8.1×10^{-2} S cm^{-1} [15], values with magnitudes greater than 10^{-4} S cm^{-1} are considered acceptable for polymeric materials for applications such as electrolytes in fuel cells [25].

FTIR analysis

Figure 5 shows the infrared spectra for each type of synthesized membrane. In the unmodified membrane, characteristic peaks to the copolymer are identified, such as CH bonds, unsymmetrical and symmetrical stretch frequencies appeared at 2967 and 2872 cm^{-1}, respectively [6]. The peak at 690 cm^{-1} shows the out of plane bending of C-H bonds in the aromatic ring [11]. Similarly C=C stretching ring at 1650-1450 cm^{-1} and C=O stretching peak at 1736 cm^{-1} [26].
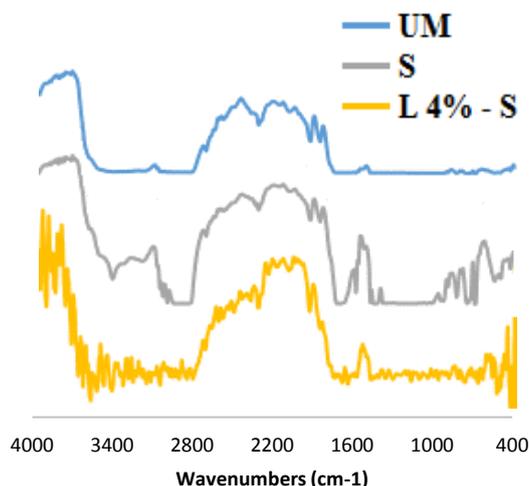
Figure 5. Infrared spectra for each membrane.

In the sulfonated and loaded-sulfonated membrane appear new peaks caused by the modifications made. The sulfonic groups are identified with the peaks in 1095 cm^{-1} and 1029 cm^{-1} assigned to asymmetric and symmetric stretching vibration of O=S=O, likewise the peak in 3465 cm^{-1} corresponding to O-H vibration [19]. In the loaded-sulfonated membrane, the peaks located between 800 and 900 cm^{-1} can be assigned to Fe-O stretching [27], in addition, a 791 cm^{-1} peak was observed attributed to the Fe-O-H bond, which indicates that the load became part of the polymer structure and did not act as a ceramic filler [28].

CONCLUSIONS

Proton exchange membranes were obtained from the n-butyl acrylate/styrene copolymer, which was modified through sulfonation and addition of ferric oxide. The FTIR analysis allowed to identify the modifications made. The results showed that the sulfonation was favorable for the copolymer since the hydrophilic character of the sulfonic groups added allowed a greater retention of water, thus improving the ion exchange capacity by forming hydrogen bonds with water molecules. The loaded-sulfonated membrane showed better characteristics for proton transport due to the joint action of ferric oxide and sulfonic groups, despite the decrease in its mechanical properties compared to the unmodified membrane, its proton conductivity indicates a good potential for the use of this membrane in fuel cells.

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