

Proton Exchange Membrane from the Blend of Copolymers of Vinyl Acetate-Acrylic Ester and Styrene-Acrylic Ester for Power Generation Using Fuel Cell

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Abstract—Proton exchange membranes for fuel cells were synthesized from the blend of copolymers of vinyl acetate-acrylic ester and styrene-acrylic ester, which were modified by sulfonation and addition of silica gel. Water uptake, ion exchange capacity, infrared spectroscopy and tensile tests were applied to characterize the prepared membranes. The results show that the prepared membranes with the processes of sulfonation and loaded with silica have the highest water uptake (92,7%). On the other hand, the sulfonation process lead to membranes with high ion exchange capacity and high mechanical strength (0,68 meq/g and 1,29 MPa, respectively). Therefore, the sulfonated membrane represents an alternative for the application as proton exchange membrane in fuel cells.

Keyword-Membrane, Proton exchange, Sulfonation, Silica gel, Fuel cells

I. INTRODUCTION

The current energy situation is based on an economically and environmentally unsustainable model since the primary energy sources are fossil fuels, non-renewable resources; due to this problematic fuel cells have generated great interest in the last decades, particularly proton exchange membrane fuel cell (PEMFC) due to their high power density, good efficiency of energy conversion and also for being a clean technology [1]. The principal component of the PEMFC is the proton exchange membrane, which is polymeric in nature; currently the most used is Nafion®, which has good mechanical properties and excellent proton conductivity. However, their use is limited by its high cost and operating temperature range [1]. These disadvantages have stimulated research to develop alternatives to improve these properties using different modification techniques and reducing the cost of fuel cells.

Sulfonated inexpensive commercial polymers have been extensively studied. Thermally stable materials with higher ion exchange capacity have been obtained using this technique in the preparation of membranes for fuel cells [2], [3]. Moreover, the production of composite membranes, which are based on solid inorganic proton conductors dispersed within the polymeric materials, such as titanium oxide, silicon oxide and zirconium oxide, have also been investigated [4]-[6], because of the possibility to control chemical and physical properties from the combination of different components. For example [7] have reported an increase in water retention when TiO₂ is added to a blend between unsaturated polyester and natural rubber. The present investigation is focused in the preparation and evaluation of proton exchange membranes from the blend between acetate - acrylic ester and styrene - acrylic ester copolymer, which was subjected to sulfonation and addition of inorganic load processes to modify the electrochemical properties of the resulting membranes.

II. MATERIALS AND METHODS

A. Materials

A blend between vinyl acetate-acrylic ester (PVA-Vinyl acrylic) and styrene-acrylic ester (RECOL® CRYL) were used, both manufactured by Re-col. Distilled water and styrene were used as solvents. Acetic anhydride 98% (manufactured by Carlo Erba) and sulfuric acid 95-97% (manufactured by MERCK) were used in the sulfonation process. The silica gel was used as inorganic filler.

B. Membrane Synthesis

Initially 10 g of each copolymer were diluted in 100 ml of distilled water; both solutions were mixed through constant stirring obtaining the unmodified blend (*U*). The loaded membranes (*L*) were prepared by adding 5% of silica gel to the unmodified copolymer solution; the resulting solution was stirred for one hour. For the sulfonation reaction, acetyl sulfate was used as sulfonating agent [8]; it was added to copolymer sample and allowed to react for three hours. Then, methanol was added to stop the reaction. Subsequently, the polymer was filtered, washed and dissolved in styrene to obtain sulfonated membranes (*S*). In the case of hybrid membranes

(sulfonated and loaded membrane, (SL), silica gel was added after dissolving the sulfonated product and the solution was allowed to stir for an additional hour. The solutions obtained from the modification processes were transferred to petri dishes and allowed to dry for 2 days.

C. Membrane Characterization

1) *Water Uptake*: The dry samples were weighed and then immersed for 24 hours in a container with distilled water at room temperature. Then the samples were taken from the containers and surface water was removed with absorbent paper, to obtain the wet weight. The percentage of water retention is calculated by the following equation [9].

$$\text{Water uptake (\%)} = \left(\frac{W_w - W_d}{W_d} \right) * 100 \quad (1)$$

where W_w is the weight after immersing the samples in water and W_d dry weight, respectively.

2) *Ion Exchange Capacity (IEC)*: The ion exchange capacity of the membranes was evaluated using a classical method of titration. The membranes were immersed in a 1 M HCl solution for 24 hours to bring them to protonic form, and then they were washed with large amounts of distilled water to remove excess acid. Subsequently the membranes were placed in a 0.1 M NaCl solution for 24 hours, and then the solution was titrated with 0.01M NaOH. The ion exchange capacity was calculated using the following relation [10].

$$\text{IEC (mequiv/g dry membrane)} = \frac{V_{NaOH} * [NaOH]}{m} \quad (2)$$

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.

3) *Mechanical Properties*: The mechanical properties of the membranes were measured using a Universal Tester EZ - S Shimadzu, at a crosshead speed of 250 mm/min. The samples were carefully cut into a size of 25 mm x 70 mm, with a thickness of 0.03 mm, which was needed for the calculation of tensile strength.

4) *FTIR Spectroscopy*: Fourier-transform infrared (FTIR) spectra were used in this study to verify the interaction between the sulphonic acid groups and the loads on the polymer matrix. The test was conducted on a Nicolet 6700 Fourier Transform Spectrophotometer, obtaining the spectrum in the range of 500 - 4000 cm^{-1} .

III. RESULTS AND DISCUSSION

D. Water Uptake

The water uptake capacity of each prepared membrane is shown in Fig. 1. All modified membranes have higher value than the unmodified membrane (U). The sulfonated membrane (S) has a water uptake of 56.8%, which is attributed to the introduction of sulfonic groups into the polymeric material by the process of sulfonation; these HSO_3^- groups have a polar nature which stimulates water uptake [11]. Similar results have been reported for sulfonated polymers [10], where an increase of water uptake capacity in the membranes increases the degree of sulfonation.

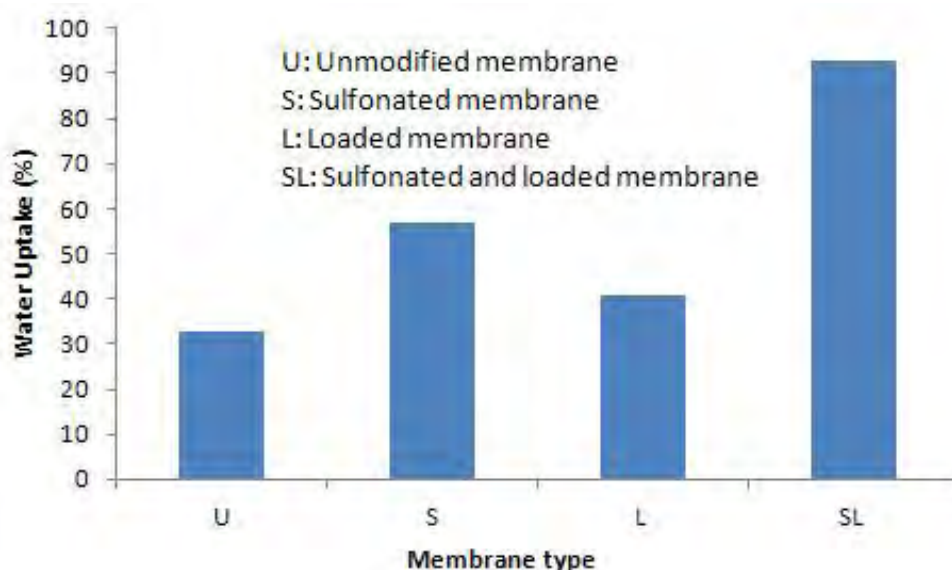


Fig. 1. Water uptake of membranes synthesized

The introduction of the inorganic load also increased the water uptake, until a value of 40.7% for the loaded with silica membrane (*L*) and 92.7% for the sulfonated and loaded membrane (*SL*), attributed to the hygroscopic effect of the group Si-OH. Also, silica increases the surface area, which stimulates the adsorption of water [6]. Additionally, the *SL* membrane has sulfonic group in its structure, which explains the high value of water retention.

E. Ion Exchange Capacity (IEC)

The results showed an increase in the ion exchange capacity of sulfonated membrane in relation to the unmodified membrane (Fig. 2). This is attributable to the loaded sites with HSO_3^- , which bind strongly to adsorbed water on the surface of the membrane, facilitating the transfer of protons across the free volume of a loaded site into another [12]. It should also be noted that the ion exchange capacity is closely related to the water uptake capacity of the membrane, because the adsorbed water acts as a carrier for the transport of protons, which is mainly through two mechanisms referred to as vehicular and Grotthuss mechanisms. In Grotthuss mechanism protons are transferred through the free volume of a place loaded to another, and on the vehicle mechanism hydrated protons (H_3O^+) diffuses through the aqueous medium in response to an electrochemical difference [12]. According to this theory, the sulfonated membrane presents a high ion exchange capacity due to the presence of sulfonic groups as proton donors, which have a high water absorption capacity.

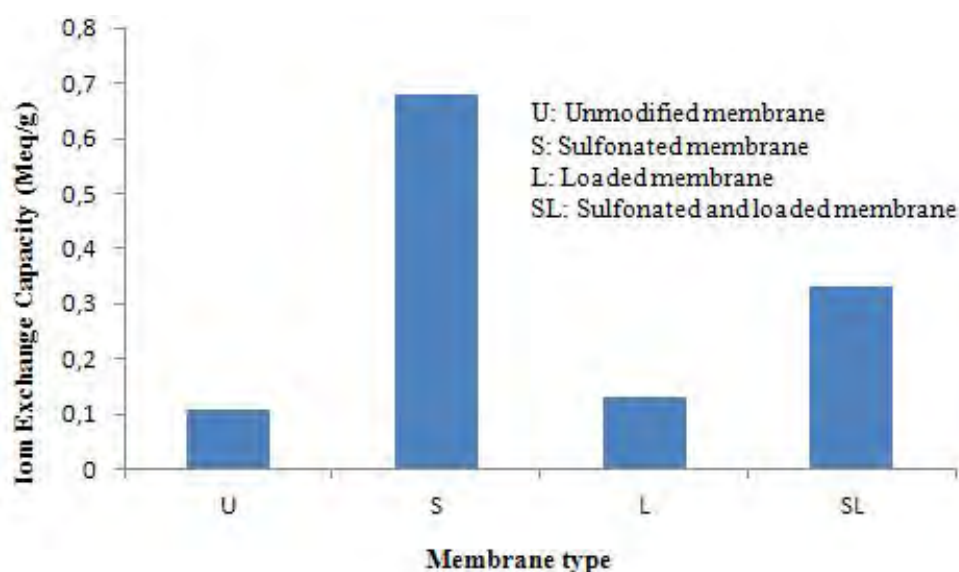


Fig. 2. Ion Exchange capacity of membranes synthesized

The ion exchange capacity of membrane loaded with silica is similar to the unmodified membrane, whereas sulfonated membranes increase significantly the ion exchange capacity, this is due to the increase of sites available for the conduction of protons into polymer network by the presence of sulfonic groups [13], which are transfer agents of the Grotthuss mechanism. However, the *IEC* of sulfonated membrane is higher than loaded and sulfonated membrane which could be caused by the agglomeration of silica particles that represents a barrier to the transport of protons [14]. This is consistent with that reported by [15], when the *IEC* of the sulfonated-loaded silica membranes prepared resulted to be lower than that obtained by the sulfonated membrane; this property decreases with increasing quantity of silica in the sulfonated membranes.

F. Mechanical Properties

Figure 3 shows maximum tensile strength and maximum elongation for prepared membranes. The maximum tensile strength was improved by the process of sulfonation, (1,29 MPa for sulfonated membrane and 1,65 MPa for sulfonated - loaded membrane). This is attributed to the strong ionic interactions of sulfonic acid groups, which increase the interactions between the molecular chains and restrict the movement of the main chain of the polymer, creating a greater tensile strength during stretching [16]. A similar trend was reported by [17], who obtained a higher mechanical strength in sulfonated membranes compared to non sulfonated membranes, which indicated that the grafted sulfonic acid groups in the polymer material reinforced this property.

The membrane loaded with silica presented a lower tensile strength (0.73 MPa) than the unmodified sample (0.76 MPa), which could be due to inhomogeneous distribution of the silica in the polymer [17]. The tensile strength of the membranes prepared is lower compared to the Nafion® membrane NRE 211-10 (8.3 MPa) under the same conditions. However, in other investigations have found membranes with values of maximum tension lower than Nafion membrane values, which have been used in fuel cells [19], [20].

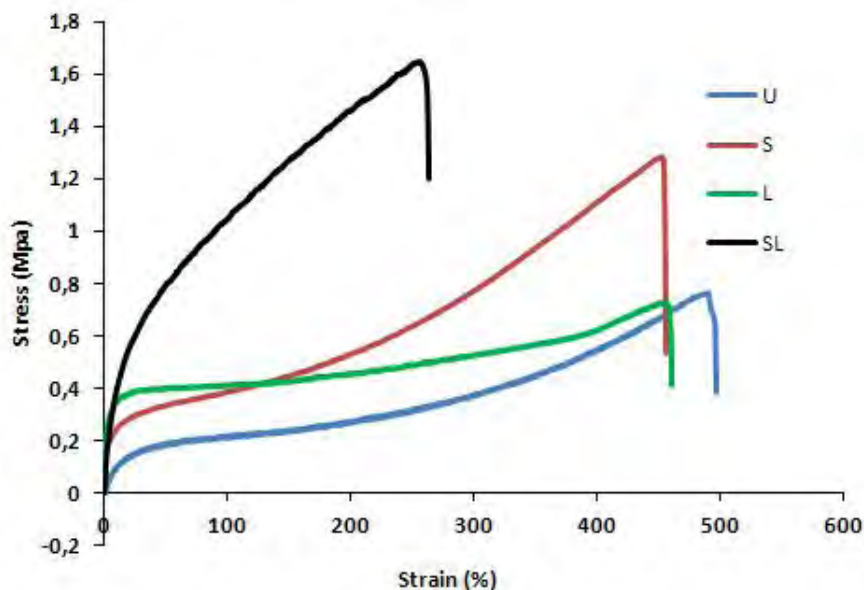


Fig. 3. Stress – strain curve of membranes synthesized

G. FTIR spectroscopy

Figure 4 shows the spectra of the samples in the range of 500-4000 cm^{-1} . In the FTIR spectrum several bands can be observed, that are characteristic of each the polymers present in the blend. A high intensity peak at 1728 cm^{-1} can be noticed, which is due to the stretching vibration of the carbonyl group (C = O) present in esters. In the region between 1558 - 1500 cm^{-1} , four bands related to the vibration of the C = C bond of the aromatic ring are observed. Around 1228 cm^{-1} , a high intensity peak, attributed to the single bond between carbon and oxygen (C-O) is shown. At 759 and 697 cm^{-1} two bands associated to the benzene group can be seen, due to the single substitution of benzene present in the styrene units and the second deformation of the benzene ring [21].

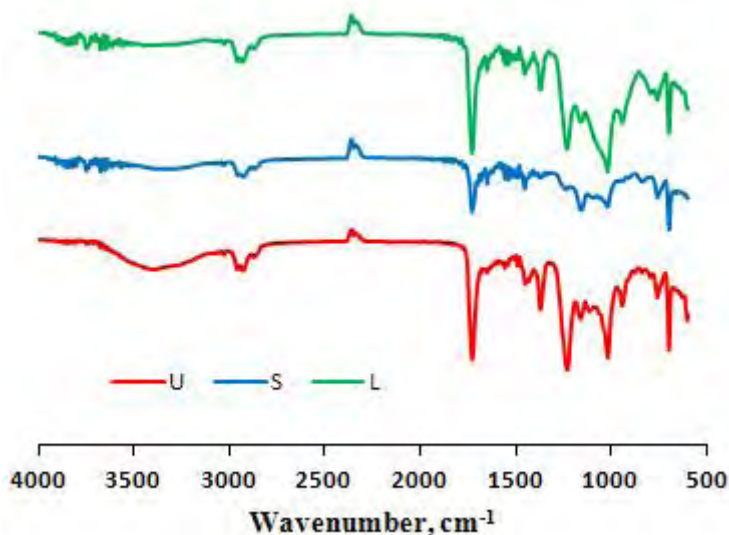


Fig. 4. IR spectra of membranes synthesized

Comparing the differences between the spectra of the samples modified by sulfonation, several changes can be seen in the chemical structure of the material. A new frequency around 1090 cm^{-1} and 1035 cm^{-1} appears in the sulfonated membrane attributed to asymmetric vibration and symmetric stretching of SO_3H groups, respectively [22].

The FTIR of the membranes modified with silica gel did not register bands, at the region between 1100-1050 cm^{-1} , characteristic of the bonds formed between the silica and the oxygen O-Si-O, due to the SiO_2 is dispersed within the material without creating actual molecular interaction with the copolymer.

IV. CONCLUSION

In the present investigation the blend between acetate-acrylic ester and styrene-acrylic ester was modified by sulfonation and the addition of silica gel. The introduction of the inorganic load was favorable for the adsorption of water due to the hygroscopic nature of the silica gel. However, excessive silica amounts can cause agglomeration of the particles, affecting the mechanical properties due to the lack of homogenization inside the material. Meanwhile, the sulfonation process also increased water uptake capacity and ion exchange as a result of the introduction of sulfonic groups. Additionally, the sulfonation process permits to obtain membranes with good mechanical resistance, due to strong ionic interactions produced by the group HSO_3^- . Finally, the results obtained suggest high potential for the application as proton exchange membrane for fuel cells.

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