Synthesis of Proton Exchange Membranes from Acrylic Ester and Styrene Resin

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Abstract— **In this work, an styrene-acrylic ester copolymer resin was used to synthesize proton exchange membranes for its application in fuel cells. The properties of these membranes were modified by the sulfonation reaction at different times. Furthermore, the water uptake, ion exchange capacity and mechanical properties were measured. Sulfonated membrane during 3 h exhibited high water uptake and proton exchange, 38.10% and 0.24 meq/g, respectively; while unmodified membranes exhibits low water uptake and proton exchange, 16.08% and 0.1 meq/g respectively. Moreover, elasticity of the membrane increases with increasing the sulfonation reaction time due to the introduction of sulfonic groups into the polymer chain. The properties of membranes confirm the possibility of its use as a proton exchange membrane.**

KEY WORDS: Proton exchange membrane, acrylic ester and styrene, sulfonation.

INTRODUCTION

Accelerated energy consumption worldwide will lead to the depletion of oil fields which represents its main raw material. Therefore, it is necessary to find new ways of generating cleaner and renewable energy that ensures sustainable development. The fuel cells of proton exchange membrane are a viable alternative for finding better energy sources that replace fossil fuels. These are electrochemical devices that convert the energy contained in a fuel directly into electricity, without the need to undergo a pre-burn [1-2].

Fuel cells of proton exchange membrane require a membrane for separating the chemical reactions of the anode and cathode. Commercial prototypes of perfluorinated polymers exist, but they present difficulties operating at temperatures above 80 ° C since they require humidification of 100% [3]. Therefore, one of the areas of interest in these cells is the development of low-cost membranes for applications at high temperatures (T> 100 ° C) using hydrogen or methanol as a fuel.

Operating at high temperature has great advantages such as improving the reaction kinetics of the electrodes, less consumption of catalytic metal and so on [4-5].

The purpose of the following work is to prepare proton exchange membranes from the styrene - acrylic ester resin through sulfonation reactions at different times and evaluate its water uptake and proton exchange capacity.

1. MATERIALS Y METHODS

The resin used for the development of this research was acrylic ester styrene resin distributed by the company RECOL under the name RECOL ® CRYL. Distilled water, acetic anhydride, sulfuric acid, hydrochloric acid, sodium hydroxide, methanol and styrene were used as reactives for the preparation and characterization of the membranes, provided by the University of Cartagena, Colombia.

1.1. Unmodified Membranes

Figure 1 shows the procedure for the preparation of unmodified membranes. In a beaker were dissolved 10 g of the resin in 40 ml of distilled water under stirring for 5 min. Then, the solution was poured into Petri dishes, for the formation of the films and subsequent demolding.

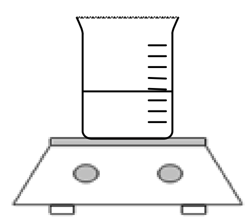

Fig. 1 Preparation process of unmodified membranes.

1.2. Sulfonated Membranes

10 g of the resin styrene - acrylic ester are poured into a plane bottomed flask and dissolved in 100 ml of distilled water for 15 min. Moreover, the sulfonating agent used is acetyl sulfate, which is prepared as follows: 100 ml of distilled water is cooled in an ice bath for 10 min, then 4.7 ml of acetic

anhydride is added and wait for the solution to be cooled for another 10 min and finally 2.7 ml of sulfuric acid is added dropwise to the resin solution and let the reaction to occur for each defined time (2 h and 3 h). Figure 2 shows the schematic of sulfonation reaction.

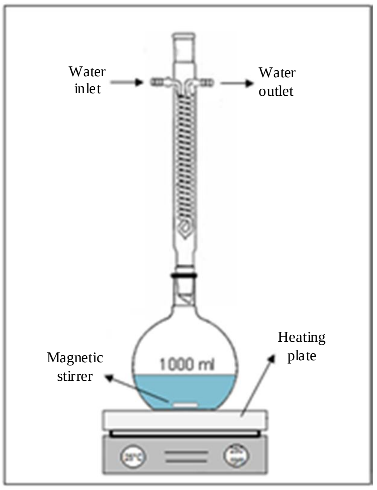

Fig. 2 Schematic of sulfonation.

Once the sulfonation time has ended, the reaction is stopped using 100 ml of methanol, whereupon the polymer collected is filtered, dried and dissolved in styrene to be poured into petri dishes, where the solvent is evaporated and the film is formed [6].

2. CHARACTERIZATION OF MEMBRANES

For the characterization, each membrane type was tested for water uptake capacity, ion exchange capacity and tensile strength.

2.1. *Water Uptake Capacity*

Each type of membrane was divided into 4 sections of 2 cm by 2 cm, were dried in an oven at 35 ° C for one hour to remove humidity in excess, and then the dry weight is determined; each sample was immersed in 50 ml of distilled water for a period of 24 hours. After, the samples were removed; surface water is eliminated and weighed again. The difference between wet and dry weight provides the water uptake capacity which is calculated by the following equation [7].

$$Water\ Uptake, \% = \frac{wet\ weight - dry\ weight}{dry\ weight} \times 100$$

2.2. *Ion Exchange Capacity*

Membrane was divided in four samples of 2 cm by 2 cm, and the samples were immersed in a 1M solution of hydrochloric acid for 24 hours. Then, samples are removed and added to a 0.1M NaCl solution for 24 hours. Finally the membranes are removed and the solutions are titrated with 0.01M NaOH solution. The ion exchange capacity is calculated by the following equation [8]:

$$IEC\ (mequiv/g) = \frac{V_{NaOH} \times M}{W}$$

Where V is the volume of NaOH added to neutralize the solution, M is the concentration of NaOH, and W is the weight of the dried sample.

2.3. *Tensile Strength*

The mechanical properties of the membrane, such as tensile strength, stress, strain, were calculated with a universal testing machine EZ-S Shimadzu located in the laboratories of the University of Cartagena, Colombia.

3. RESULTS Y DISCUSSION

The prepared membranes were obtained using the procedures described in the previous section. Three types of membranes were characterized, which are shown in Figure 3.

SM S-2h S-3h

Fig. 3 Membranes synthesized. SM: Unmodified, S-2h: 2h of sulfonation reaction, S-3h: 3h of sulfonation reaction.

3.1. *Water Uptake Capacity*

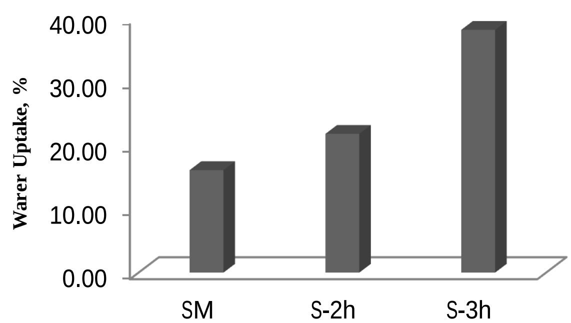

Fig. 4 Water uptake of membranes synthesized. SM: unmodified, S-2h: 2h of sulfonation reaction, S-3h: 3h of sulfonation reaction.

The sulfonation process is performed in order to increase the water retention capacity by the interaction of water with the sulfonic acid groups of the polymer molecule, which enables migration methods in the proton exchange membrane. These are mainly the Grotthuss mechanism, in which the protons jump from hydrolyzed ionic site to another and the

mechanism of vehicles consisting in the protons transport through hydronium groups by electrochemical difference [9].
Figure 4 shows that the unmodified membrane presented a low value of 16.08%, which confirms their use as auxiliary waterproofing further feature attributed to the nature of materials. Moreover, the sulfonation time increased the water retention capacity of 21.78% for the 2h - sulfonated membrane to 38,10% for the 3h - sulfonated membrane, which represents an increase of 75.3% in the water uptake. This is the result from the presence of more number of sulfonic groups in the molecular structure, which are hydrophilic, promoting the uptake of water.

3.2. *Ion Exchange Capacity*

The proton exchange capacity gives an approximation of the acid groups having H^+ ions. These ions form weak bonds with sulfonic group and are able to pass from the anode to the cathode through the proton transfer mechanisms [10]. Figure 5 shows the results for the ion exchange capacity.

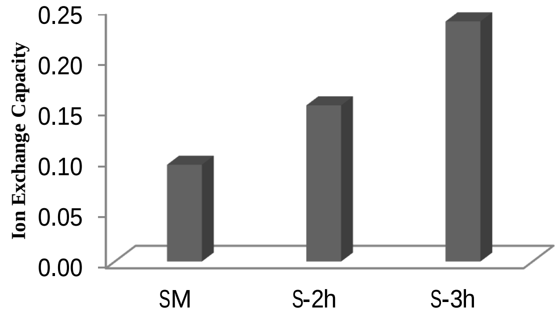

Fig 5 Ion exchange capacity of membranes synthesized. SM: unmodified, S-2h: 2h - sulfonated , S-3h: 3h - sulfonated.

The ion exchange capacity increases with increasing the sulfonation time from 0.15 meq/g (2h - sulfonated membrane) to 0.24 meq/g (3h - sulfonated membrane), due to the presence of more sulphonic groups which makes easier to the proton migration inside the membrane. Furthermore, unmodified membrane showed a lower value ion exchange (0.10 meq / g), due to the low water uptake, due to the absence of charged sites (HSO_3-) to permit the transport of protons.

3.3. *Mechanical Tests*

Figure 6 shows the tensile behavior for different deformation percent of each type of membrane, and Table 1 shows maximum stress.

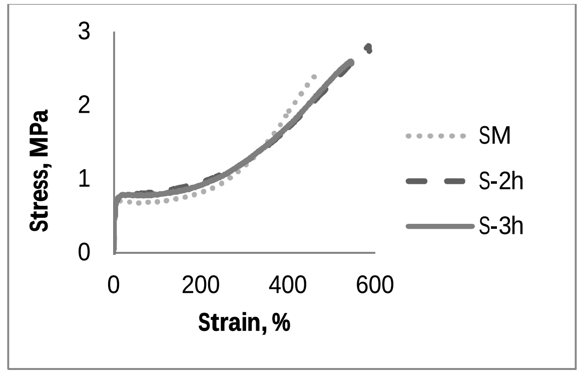

Fig. 6 Stress vs. Strain curves for membranes synthetized

Table I
Mechanical Properties of the Membranes

TYPE	MAXIMUM STRESS, MPa	MAXIMUM DEFORMATION, %
Unmodified	2,476	478,270
2h - Sulfonated	2,807	588,599
3h - Sulfonated	2,599	548,066

Sulfonated membrane exhibits higher tensile strength and elongation at break than the unmodified membrane, due to the addition of sulfonic acid groups which makes it more flexible. Moreover 3h sulfonated membrane showed a lower tensile strength compared to 2 hr sulfonated membrane, this is due to a longer time of reaction increase the degree of sulfonation i. e., there are a greater number of sulfonic acid groups in the polymer structure, which favors water retention capacity. The absorbed water acts as a plasticizer, affects the mechanical properties [11]. Romero et al. [6] prepared membranes from unsaturated polyester resin and natural rubber with similar values of maximum stress.
Mechanical properties are important because withstand the mechanical stress and the assembly process in the fuel cell [12].

CONCLUSIONS

In the development of this research, proton exchange membranes were prepared from the acrylic ester and styrene copolymer, by modifying its properties through sulfonation reactions at different times.
Sulfonated membrane has higher water absorption, ion exchange and tensile strength than unmodified membrane due to the addition of sulfonic acid groups in the polymer chain, which has hydrophilic and elastics properties. Finally, water uptake, ion exchange and tensile strength properties of membrane increase with increasing sulfonation reaction time.
The above results indicates that membranes prepared with acrylic ester - styrene copolymer have high potential for applications as proton exchange membranes in fuel cells.

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