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Synthesis of proton exchange membrane from SEPS copolymer for fuel cell applications

Baldiris-Navarro I.[1]*, Realpe A.[2], Fajardo J.[3], Mendoza D.[1], Acosta J.[1]

[1]Quality Control program, Ciptec Research Group, Engineering Faculty, Fundacion Universitaria Tecnologico Comfenalco, Colombia
[2]Department of Chemical Engineering, Research Group of Particles and Processes Modeling, Engineering Faculty, Universidad de Cartagena, Colombia

Abstract : In this paper proton Exchange membranes were synthetized from SEPS copolymer, which was modified by sulfonation reaction and addition of titanium dioxide. Membranes thickness, Water uptake, ion exchange capacity, infrared spectroscopy and performance tests in a fuel cell were applied to characterize the obtained membranes. Results showed that sulfonated and loaded membrane(2h and 2%) exhibited a thickness range of [0.0147mm - 0.0319mm], 6% of water uptake, 1.18 of ion exchange capacity, all these are due to the presence of sulfonic acid groups in the polymer chain which facilitate the proton transport mechanisms in the membrane. Additionally, the performance test showed that the fuel cell may yield a power density of 60 $mW \cdot cm^{-2}$. Therefore, the sulfonated and loaded membrane represents an alternative for the application as proton exchange membrane in fuel cells.

Keywords : Proton exchange membrane, copolymer, sulfonation, fuel cell.

I. Introduction

As the world's population approaches 9 billion people by 2040, the challenge of engineering is not only to meet basic needs but also to improve the quality of life in the world[1][2]. Energy consumption from fossil fuels is responsible for major environmental problems (global warming, acidification, etc.). It is estimated that in the last 50 years the increase in energy consumption has led to an increase in CO_2 global emissions and other greenhouse gases, reaching a level close to 30,000 million tons[3].One of the emerging alternatives to reduce CO_2 emissions are fuel cells, which are devices that use the chemical energy of a fuel for a clean and efficient way to produce electrical energy. If hydrogen is the fuel then electricity, water and heat are the only products, thus reducing CO_2 production[4].

Fuel cells include in their structure a membrane that makes possible the transport of protons. Currently, the perfluorinated membranes such as Nafion have been used widely as Proton Exchange Membranes(PEMs). Which have high proton conductivity, excellent chemical stability and good mechanical properties for PEM fuel cells operating below 80 ° C. However, they show severe deficiencies such as high cost, low conductivity at low humidity or high temperatures[5]. The objective of this work is the synthesis and characterization of proton exchange membranes based on SEPS copolymer modified by sulfonation and addition of a conductive solid (Titanium dioxide), to be used in PEM fuel cells.

2. Experimental

2.1. Materials

Copolymer and reagents used in this investigation were reactive grade. SEPS Copolymer was obtained from Kraton, Dichloromethane and Sulfuric acid were supplied by Merck. Toluene, methanol and acetic anhydride were purchased from Fisher Scientific and all used as received.

2.2. Synthesis of membranes

For the synthesis of membranes was used a multifactorial experimental design with two factors, sulfonation time and addition of load. First factor had three levels (0h, 1h, 2h) and the second one had four levels (0%, 2%, 5% and 7%), which led to the development of twelve membranes. The aim of this design was find relationships between these two independent variables and the response variables: water uptake and ion exchange capacity.

2.3. Unmodified membranes

Seven grams of SEPS copolymer were measured, then 70 ml of toluene were added to the polymer, the solution was stirred for two hours at 40 ° C. Then, samples were deposited into Petri dishes, for the formation of the films and subsequent demolding.

2.4. Sulfonation process

First a sulfonating agent solution was prepared,this solution must remain in ice bath at a temperature of about 0 ° C. To prepare this solution 100 mL of dichloromethane were added in a beaker and refrigerated, after ten minutes were added 4.73 mL of acetic anhydride, after10 minutes 2.68 mL more of sulfuric acid were added. Before this seven grams of SEPS were solubilized in 100 ml of dichloromethane. When sulfonating agent was ready it was added to the polymer. The Mixture was kept under stirring and deposited on a precipitate balloon connected to a condenser for 2 hours, after this time the reaction was stopped with 100 mL of methanol, then the solution on the balloon was filtered and the sulfonated polymer was obtained.

2.5. Loaded membranes

Was prepared a solution with the conductive solid and an organic solvent, in this case the solvent was toluene and a the solid was Titanium Dioxide. After obtaining the solubilized filler solution in toluene as mentioned, 7 g of the SEPS copolymer were added to the mixture. The mixture was then stirred and heated for two hours at 40 ° C, then the content was deposited in a Petri dish, in order to obtain the film of the SEPS copolymer loaded with particles of titanium dioxide.

2.6. Sulphonated membranes

After obtaining the sulfonated copolymer and a purification process with distilled water and deionized water to remove the reactants and neutralize pH, the polymer was passed through a furnace for 24 hours at 60 ° C in order to guarantee the total elimination of the reagents. The dried polymer was then immersed in 70 ml of toluene, then was stirred and heated to a temperature of 40 ° C, then the mixture was transferred to a Petri dish for 24 hours until the toluene was evaporated.

2.7. Sulfonated-loaded Membranes

To obtain this kind of membranes, to the solution titanium dioxide and toluene was added the sulfonated copolymer, this mixture was stirred at 40 ° C until homogeneity. Then the solution was poured into Petri dishes and sulfonated-loaded membranes were obtained.

3. Characterization

3.1. Membranes thickness

To measure thickness of the membranes was used a Vernier Redline Mechanics with an error of +/- 0.01 mm. Measurements were made at nine different points around the membranes to verify the homogeneity of the membrane thickness. According to authors the values of this parameter should vary between 30-200 um[6][7]

3.2. Water uptake

Water uptake was calculated by setting the weight difference between dry and wet membranes. Dry membranes were weighed first and then immersed in deionized water at room temperature for 24 h. The membranes were then taken out, wiped off the surface water with blotting paper and wet weight was weighed[8]. The percentage of water retention was calculated by the following equation:

$$\text{ater uptake} = \frac{w_{wet} - w_{dry}}{w_{dry}} \text{ x } 100\% \qquad (1)$$

3.3. Ion exchange capacity

Ion exchange capacity (IEC) was evaluated by titration. Dried membranes in the protonic form was immersed in 1 M NaCl solution for 24 h at room temperature. The H^+ ions,substituted by Na^+ ions, were released into the solution. The solutionwas then titrated by a 0.012 M NaOH solution using phenolphthalein as indicator. The IEC of the membranes werecalculated using the following equation-

$$IEC_{\left(\frac{meq}{g}\right)} = \frac{V_{NaOH} x C_{NaOH}}{w} \qquad (2)$$

whereV_{NaOH} is the volume of NaOH added during titration, $C_{NaOH}$is the molar concentration of NaOHywis the dry sample weight[9].

3.4. Fourier transform infrared spectroscopy

FT-IR analysis was perform using a SHIMADZU 8400 S spectrophotometer, obtaining an infrared spectrum in the range of wavelengths between 400 y 4000 cm-1[10][11].

3.5. Fuel cell performance

A MEA was fabricated with the obtained membrane and between two electrodes and two gas diffusion layers (GDLs). then, a Performance test with the MEA was carried out using a lab fuel cell test system, using H_2 as fuel and dry air as oxidant (134 and 362 mL min−1, respectably). The tests were run at atmospheric pressure, 70 °C cell temperature and 70%RH[5][12].

4. Results and Discussion

4.1. Thickness

Membranes thickness are shown in Fig. 1. Membranes with 2h-2%, 2h-5% y 2h-7% processes were the ones with lower thickness, similar to those used by other authors, which may be an important factor for the conduction of protons in a fuel cell test.

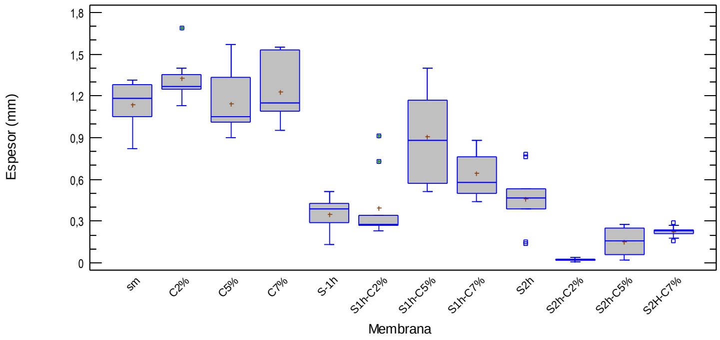

Fig.1. Box plot for membranes thickness

4.2. Water uptake

Fig. 2shows that Sulfonation process enhance water uptake capacity, due to the introduction of sulfonic groups into the copolymer. These groups increase the hydrophilic region in the membrane due to its polar nature [13].

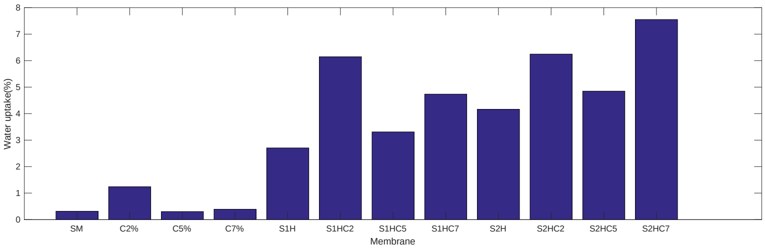

Fig. 2 Variación de la absorción de agua en las membranas sintetizadas

Membranes S(1h)-C(2%), S(2h)-C(2%) y S(2h)-C(7%), obtained the highest values for water uptake, but these values are lower than Nafion's[11], this might be possibly remedied if reactant gases are humidified during the cell operation.

4.3. Ion exchange capacity (IEC)

Membranes IEC assays were performed by triplicate andthe results are depicted in Fig.3.

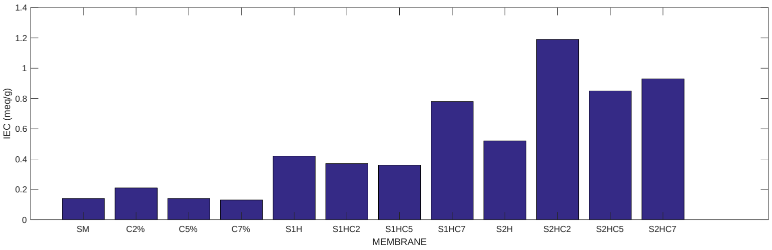

Fig. 3IEC variations for synthesized membranes

Two hours sulphonated membranes and loaded with 2%,5% y 7% showed highest IEC values [1.18, 0,85 y 0,93 meq/g respectively], the last two values are similars to nafion's, but 2% doped one had the highest and it is higher than nafion's, which is a good signal for the conductivity of protons in a fuel cell test. Titanium dioxide gives rise to bonds Ti-OH with water in the Surface of membranes, which due to OH- groups enhance water uptake and also the amount of ionic exchange points in the membrane (-HSO_3), which improves IEC[14].

4.4. Infrared Spectroscopy

The chemical structure of the membrane with two hours (2h) of sulfonation and 2% of load concentration (2h-2%) treatment, was investigated by FT-IR, in the range of 500-4000 cm^{-1}

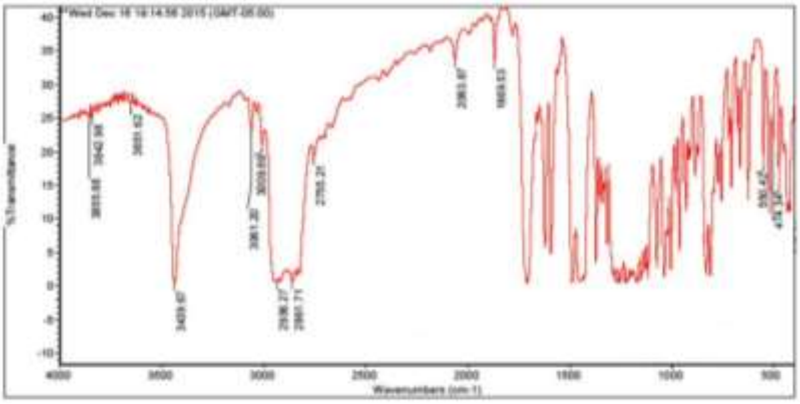

Fig. 5. FT-IR spectra for 2H-2% membrane

In Fig.5 are shown the peaks after the sulfonation process, some of them are at 1227 cm^{-1}, 1085 cm^{-1} and 1021 cm^{-1} representing stretching, symmetrical stretching and asymmetric stretching of the sulfonic group ($-HSO_3$), this indicates that sulfonation process had the desired effect on the copolymer. In the case of titanium dioxide, peaks appear in the range 450 - 550 cm^{-1} as shown in the spectra. The peaks at 605 cm^{-1} and 3619 cm^{-1} indicate the presence of Ti-O and OH^- groups. In addition, the peaks of the copolymer structure, 711 cm^{-1} for styrene, 908 cm^{-1} for ethylene and 1462 cm^{-1} for propylene are also shown by the spectra [9][11].

4.5. Cell performance

MEA was fabricated with a membrane between two electrodes for anode a cathode and between two gas diffusion layers (GDLs). The membrane of two hours of reaction (2h) and 2% of load concentration, which has a thickness of [0.0147mm - 0.0319mm], a water uptake percentage of 6.25% and an ion exchange capacity of 1.60 meq · g^{-1} was tested in a fuel cell at 70 ° C and 1 atm, values are shown in Fig.6.

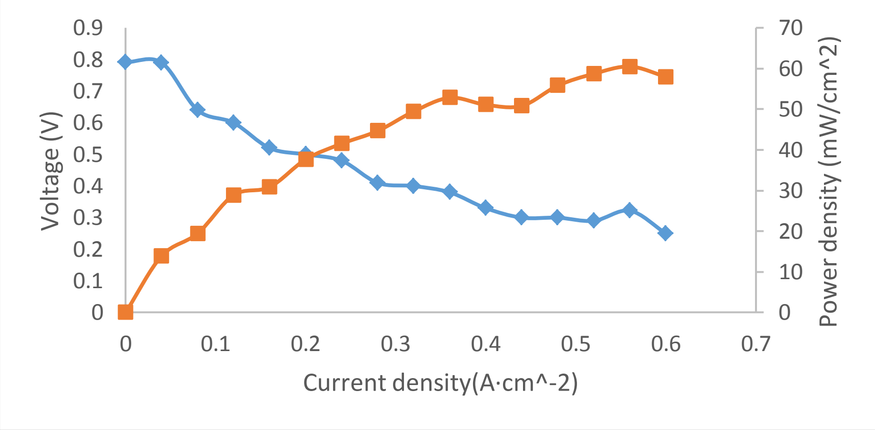

Fig. 6. Polarization curveand power density curve

Membrane yielded a power density around 60mW·cm^{-2}, obtained power density is lower thanobtained in other studies[12][15][16], who reported values between 600 y 4000 mW·cm^{-2}. A factor that could influence the cell performance was the MEA compaction, since it must be compressed at a high temperature (100-140 ºC)as proposed by other authors[17][7]. Cell Performance may also be improved by using electrodes with a higher concentration of platinum as catalyst.

5. Conclusions

According to FT-IR test sulfonation and loading processes were successfully performed on the membranes to improve their properties.The thickness characterization showed that the membranes with the lowest thickness were those subjected to sulfonation reaction. Among these sulfonated two hours and loaded at

2%, 5% and 7% showed better values of this variable. The loaded membranes presented high values, which is not favorable for the performance of the membranes. Copolymer sulfonation increased the polarity of the membrane due to the presence of the sulfonic groups, this was reflected in the increase of up to 7% in water uptake with respect to the unmodified membrane.Ion exchange capacity was also improved by sulfonation and loading processes, reaching values of 1.18 meq / g for the membrane of 2h-2% much higher than that of commercial membranes which is 0.89 meq / g. This evidence the importance of the groups introduced into the polymer in the transfer of protons within the membrane.MEA was assembled manually in the laboratory and successfully operated in the fuel cell. It was observed that membrane achieved a power density of around 60 mW · cm-2,obtained power density is lower than obtained in other studies and smaller than that developed with Nafion, which is the commercial membrane. Based on the characterizationresults, sulfonated andloaded membranes of SEPS copolymer have high potential as electrolyte for proton exchange membranes fuel cells.

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