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Effect of the Sulfonation on Proton Exchange Membrane Synthesized from Polyvinyl Alcohol for Fuel Cell

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Abstract

Proton exchange membranes were synthesized from the Polyvinyl Alcohol copolymer (PVA) crosslinked with potassium hydroxide (KOH) and formaldehyde (CH_2O), and sulfonated in 1, 2 and 3 hours of reaction to evaluate their application in fuel cells. The physicochemical and mechanical properties of the membranes were characterized. The results show that the membrane sulfonated at 3 hours presented the highest ion exchange capacity (1.19 meq/g) and a very good water retention (240%), due to the hydrophilic character of the sulfonic groups added to the polymer matrix, while the mechanical properties decline with respect the unmodified membrane and the FTIR tests confirmed the presence of the sulfonic groups ($-SO_3H$) in the polymer. These results demonstrate acceptable characteristics of the prepared membranes to be used in fuel cells.

Keywords: Polymer membrane, Sulfonation, Polyvinyl Alcohol, Fuel Cell.

INTRODUCTION

Currently fossil fuels have become the main source of energy production worldwide [1], which has originated environmental problems that have accelerated global warming, due to greenhouse gas emissions to the atmosphere at an alarming rate. To counter this environmental negative impact, clean energy sources were proposed, such as hydrogen fuel cells, which converts chemical energy of hydrogen into electrical energy and produces only heat and water [2-3]. Proton exchange membrane fuel cells (PEMFC) are one of the most promising technologies for delivering clean and efficient power to automotive and residential applications [2]. 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 [3]. In order to overcome these drawbacks, recent research has focused on the development of a polymer or polymer mixtures with low cost, long life and easy recycling to avoid environmental damage [4].

In the present work the synthesis of polymeric membranes was made from the Polyvinyl Alcohol copolymer (PVA) which was modified by sulfonation in different times of reaction to evaluate its effect on the physicochemical and mechanical properties of the membrane.

MATERIALS AND METHODOLOGY

Materials

Polyvinyl Alcohol was used (PVA, 99.8% hydrolyzed, MW = 77.000-79.000 g/mol) purchased through JT Baker, potassium hydroxide, formaldehyde, sulfuric acid, acetic anhydride and methanol. Deionized water was also used as solvent for the preparation and characterization of the membranes.

Methodology

An unmodified membrane was prepared and three other were sulfonated during 1, 2 and 3 hours of reaction. In the first instance, 6 g of granule PVA were added slowly, using good agitation, to 180 mL of cool water (15-20°C). Then to complete dissolution the temperature was increased to 93-95 °C with a hold time of 40 minutes [5]. After this time, 0.03 mL of CH_2O and 0.018 g of KOH were added to the solution, the temperature was decreased to 80 °C and left in continuous agitation for 24 hours to cross-link the membrane [6]. The final solution was divided into 4 aliquots of 40 mL; the first one was dosed in a petri dish to obtain the unmodified membrane, allowed to stand at room temperature for 3 days while the water evaporated. To the three other aliquots each one of 40 mL, the sulfonation process was realized as follows; acetyl sulfate was used as sulfonating agent, which was prepared from sulfuric acid and acetic anhydride, for this 100 ml of deionized water was placed in an ice bath for a time of 10 minutes, then 2.4 ml of acetic anhydride were added and after 10 minutes 1.4 ml of sulfuric acid was slowly added and was stirred slightly. Then the acetyl sulfate was added dropwise into one aliquot and stirred for 1 h while the sulfonation occurred. Subsequently, 100 ml methanol was added to stop the reaction [4]. The obtained solution was heated at 98°C to evaporate the methanol and the excess of water. Finally the resulting aliquot of was dosed in a Petri dish to obtain the sulfonated membrane during 1 h, allowed to stand at room temperature for 3 days and carried into a laboratory oven for 30 minutes at 70°C to dehydrate it, obtaining a brown colored membrane. For the remaining membranes, the previously described steps were repeated, but this time the case the time of reaction changes to 2 h and 3 h.

Characterization of the membranes

The water absorption capacity of the membranes was obtained by drying samples of 1 cm^2 in an oven at 60 °C for 2 hours,

the weight of the dry membranes was taken and then distilled water was immersed for 24 hours at room temperature, after this time, the excess water was removed with absorbent paper and the weight of the wet membranes was taken [7]. The ion exchange capacity of the membranes was determined by the titration method. Samples of 2 cm^2 were dried in an oven at 60 °C for 2 hours, the weight was taken and they were immersed in a 1M solution of HCl for 24 hours at room temperature, after this time the samples were removed and they were placed in a 1M NaCl solution for 24 hours, finally this solution was titrated with 0.01 M NaOH [8]. An analysis of the mechanical properties of the membranes, as the maximum stress, maximum strain and Young's modulus was performed by a tensile test using the test equipment EZ-S Universal Shimadzu at a constant speed of 250 mm/min. Finally, the FTIR analysis was carried out, which allows to know the main functional groups of the molecular structure of a compound, where a Nicolet 6700 reference Fourier transform spectrophotometer was used to obtain the infrared spectrum in the range of lengths of wave between 4000 cm^{-1} and 400 cm^{-1}

RESULTS AND DISCUSSION

Fig. 1 shows the 4 types of membranes synthesized, each characterized by water absorption, ion exchange capacity, mechanical tests and FTIR analysis.

Water uptake capacity

Figure 2, shows the results of the water uptake of the prepared membranes. The unmodified membrane of PVA has a value of water uptake equal to 101% due to his high hydrophilic nature which is enhanced by his degree of hydrolysis that is 99.8% [9-10].

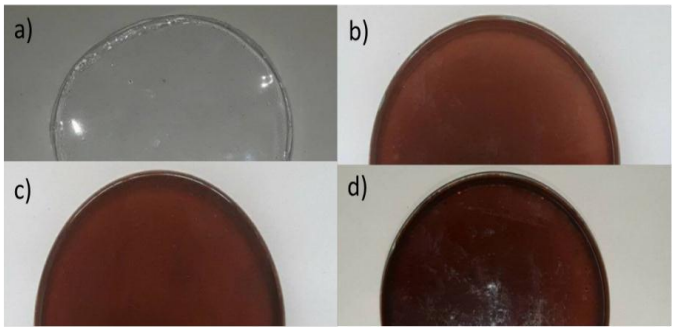

Figure 1: Prepared membranes: a) Unmodified, b) Sulfonated 1h, c) Sulfonated 2h, d) Sulfonated 3h.

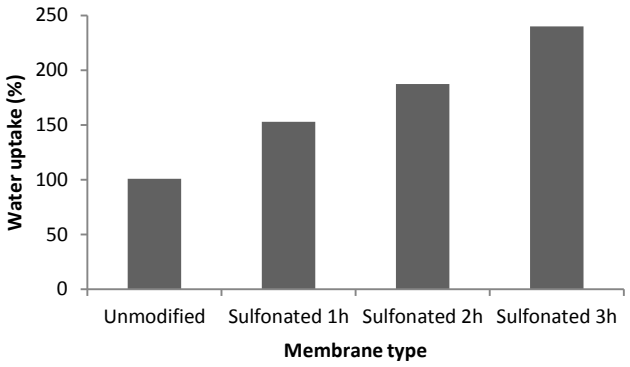

Figure 2: Water uptake for each membrane.

Regarding to sulfonated membranes, the results show that the water uptake increase with increase the time of sulfonation of the polymer matrix, staring in a value of 153% for the PVA membrane sulfonated during 1 hour and reaching the value of 240% for the PVA membrane sulfonated during 3 hours, which is due to higher affinity of the sulfonic acid groups towards hydration [11], since hydrogen bonding with water molecules occurs between the hydroxyl (–OH) and sulfonic acid (–SO3H) groups of sulfonated PVA [12].

Ion exchange capacity

Figure 3 shows that the IEC value of the unmodified membrane increase with respect to the sulfonated membranes from 1.04 to 1.19 meq/g, this property has an important relation with the capacity of water absorption, because water is a favorable medium for the two main transfer mechanisms of protons which are “jump” or Grotthuss and vehicle [13].

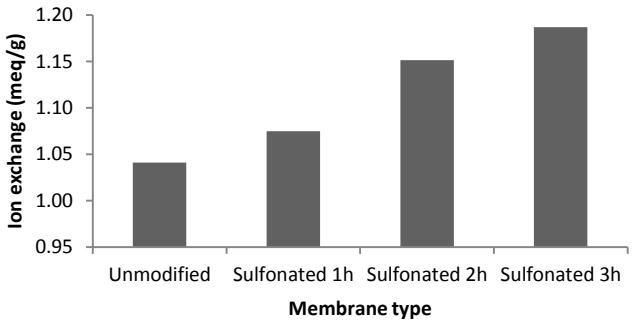

Figure 3: Ion exchange capacity for each membrane

In addition, the sulfonated membrane for 3 hours exceeds the IEC of the commercial membrane Nafion 117 by 17%. The increase in the IEC is attributed to the effect of the sulfonation reaction that introduces a greater number of SO_3H groups into the polymeric structure of the PVA [10]. Previous studies have shown that the IEC increase with the number of SO_3H groups in the polymer chain [14].

Mechanical tests

Table 1 shows the maximum tensile strength (maximum effort), the percentage of deformation reached upon reaching the break (maximum deformation) and the resistance to the given tension in the zone of linear deformation (Young's modulus) for each of the synthesized membranes. The longer the sulfonation time, the lower the maximum effort, maximum deformation and young's modulus was found for the polymer membranes. The unmodified PVA membrane exhibited a maximum effort of 18 MPa with Maximum deformation value of 262,5%. The maximum effort was reduced to 0,1 MPa and the Maximum deformation was also down to 5,8% when the membrane had been sulfonated for 3 h. This could be attributed to the reduction of traction resistance, due to the great water retention that these membranes present, which causes it to act as a plasticizer within the polymer matrix [17]. The mechanical properties were thus decreased with the increase in the time of sulfonation. However a balance between water uptake and mechanical properties could then be done to improve the traction resistance.

Analysis FTIR

Fig. 4 shows the infrared spectra obtained for each membrane. In the PVA spectrum the broad absorption band observed at 3400 cm^{-1} corresponded to the OH stretching vibrations [16], the peak at 2921 cm^{-1} is attributed to the asymmetric stretching of CH_2. Besides, at 1720 cm^{-1} is observed a peak related with the linkage of the formyl group CHO given by the formaldehyde provided by the crosslinking agent [6].

Table 1: Results maximum effort, percentage of deformation and Young's modulus.

Membrana type	Maximum effort (MPa)	Maximum deformation (%)	Young's modulus (MPa)
Unmodified	18,0	262,5	100,9
Solfonated 1h	0,2	25,1	1,0
Solfonated 2h	0,2	26,5	1,7
Solfonated 3h	0,1	5,8	1,1

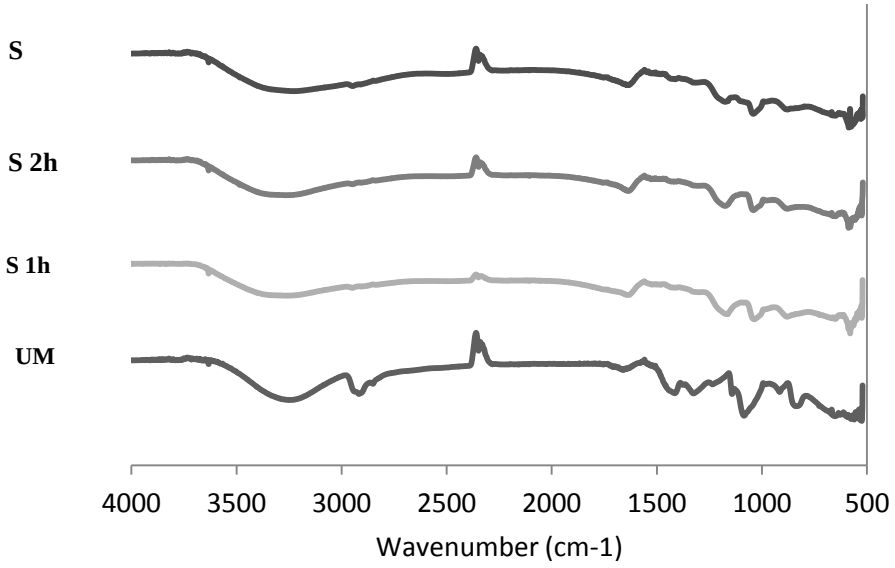

Figure 4: Infrared spectra of the unmodified membrane, sulfonated 1h, sulfonated 2h and sulfonated 3h.

The sulfonated PVA spectra were compared with the PVA, which shows, two new absorption bands at 1090 and 1040 cm^{-1}, both are ascribed to the symmetric and asymmetric stretching vibrations of O=S=O [17], the peaks at 693 and 786 cm^{-1} are due to the in-plane bending vibrations of the aromatic SO_3 groups [18]. Hence, it can be said that, the prepared membranes are properly sulfonated.

CONCLUSIONS

The characterization of the properties of the proton exchange membranes, synthesized from the polyvinyl alcohol copolymer (PVA) was carried out and modified by sulfonation. The ion exchange and water uptake capacity improve when increase the time of sulfonation showing better results for the membrane with 3 hours of sulfonation. The FTIR test corroborated the presence of the sulfonic groups (-

SO_3H) in the polymer matrix. On the other hand sulfonated membranes showed a decline in mechanical properties. In general the sulfonation improved the characteristic properties of the membrane and presented values similar to those of the commercial membrane Nafion 117 except for the mechanical properties. Therefore a balance between water uptake, ion exchange capacity and mechanical properties could then be designed to meet the requirements for it application as electrolyte of proton exchange in fuel cells.

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