Synthesis of a Proton Exchange Membrane

from Polyvinyl Alcohol (PVA)

Modified with Va_2O_5 for Fuel Cells

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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 loaded with vanadium pentoxide in amounts of 0.5%, 1.0% and 1.5%
to evaluate their application in fuel cells. The physicochemical and mechanical
properties of the membranes were characterized. The results show that the
membrane loaded at 1.5% presented the highest ion exchange capacity (1.1 meq/g)
and a very good water retention, due to the optimum level of load achieved,
allowing a correct interaction between the Va_2O_5 and the polymer matrix, while the
0.5% loaded one showed better mechanical properties (maximum stress of 35.9
MPa, maximum deformation of 218.9%, Young's modulus of 135.4 MPa) and the
FTIR tests confirmed the presence of Va_2O_5 in the polymer. These results
demonstrate adequate characteristics of the prepared membranes to be used in fuel
cells.

Keywords: Polymer membrane, Vanadium pentoxide, Polyvinyl Alcohol,
Load, Fuel Cell

1. Introduction

Nowadays, there are numerous problems related to climate change such as sea
level rise, increase in the average temperature of the earth, fracture and thaw of

polar masses, among others [1]. Excessive use of fossil fuels as a primary energy source has contributed exponentially accelerating these natural processes due to the increased generation of greenhouse gases in recent decades [2]. In order to reduce the dependence on fossil fuels, alternatives have been developed that allow the generation of energy in a cleaner way, within this group are the fuel cells, which transform chemical energy into electrical energy and are classified as having consider the type of fuel, the electrolyte and the operating temperature [3]. Proton exchange membrane fuel cells (PEMFC) are characterized by using hydrogen as a fuel [4] and utilizing a polymeric material as an electrolyte, these stand out for their high efficiency [5], the non-generation of polluting gases [6] and water as the only product in the process [7]. The PEMFCs consist basically of an anode, a cathode and an electrolyte as main components, where electricity, that is, the flow of electrons goes from the anode to the cathode following an external circuit [8]. Currently, Nafion® reference membranes are the most marketed due to their high proton conductivity, excellent mechanical properties and good chemical stability [9], however, they have high production costs, low conductivity at low humidity and loss of mechanical stability at high temperatures [10], which led to new investigations to find a polymer or polymer mixtures that have suitable properties for application in fuel cells [11]. The addition of metal oxides to the polymeric material tends to improve some of its properties, such as water retention and ion exchange [12], as well as the thermal and chemical resistance of the membrane [13].

In the present work the synthesis of polymeric membranes was made from the Polyvinyl Alcohol copolymer (PVA) which was modified with vanadium pentoxide load in different proportions to evaluate its effect on the physicochemical and mechanical properties of the membrane.

2. Materials and Methodology

2.1 Materials

Polyvinyl Alcohol was submitted (PVA, 99.8% hydrolyzed, MW = 77.000-79.000 g/mol) by JT Baker. Potassium hydroxide, formaldehyde, vanadium pentoxide (Va_2O_5), hydrochloric acid, sodium chloride, sodium hydroxide were submitted by University of Cartagena, as well as deionized water as solvent for the preparation and characterization of the membranes.

2.2 Methodology

An unmodified membrane was prepared and other three membranes were loaded with vanadium pentoxide (% w/w) at 0.5%, 1.0% and 1.5%. In the first instance, 3g of PVA were dissolved in 80 mL of deionized water at a temperature of 70 °C for 24 hours with continuous agitation. After this time, 0.03 mL of CH_2O and 0.018 g of KOH were added to the solution, the temperature was increased to 80 °C and left in continuous agitation for 24 hours to cross-link the membrane [14].

The final solution was divided into 2 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. While the second aliquot was added the 0.5% load corresponding to 0.0075 g of Va_2O_5, it was left in agitation for 5 hours, then it was dosed in a Petri dish and a drying procedure similar to the first membrane was followed. For the remaining membranes, the previously described steps were repeated, but this time the first aliquot was added with 0.015 g of Va_2O_5 and the second with 0.0225 g of Va_2O_5, which represents the load of 1.0% and 1.5%, respectively.

2.3 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 (W_s) 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 (W_h).

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, applying the equation (1) and the ion exchange capacity expressed in meq/g was obtained.

$$IEC\ (meq/g) = \left(\frac{C_{NaOH} - V_{NaOH}}{W_s} \right) \tag{1}$$

where C_{NaOH} is the concentration of NaOH (mol/L), V_{NaOH} (mL) represents the volume of NaOH used in the titration and W_s (g) is the weight of the dry membrane [15].

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}.

3. 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.
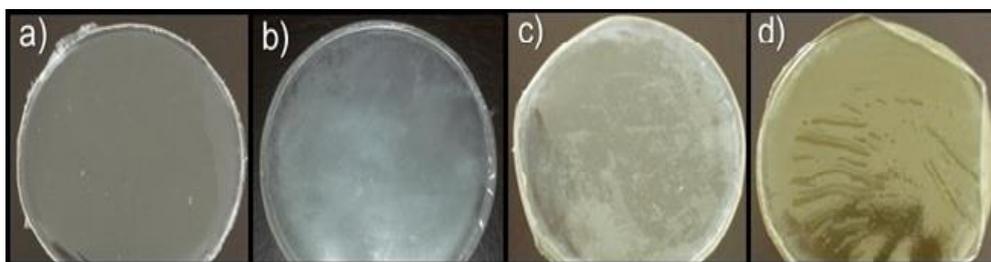
Fig. 1: Prepared membranes: a) Unmodified, b) Loaded 0.5%, c) Loaded 1.0%, d) Loaded 1.5%.

3.1 Water absorption capacity

In Fig. 2 it is observed that the unmodified membrane shows water absorption of 101.1% due to the high degree of hydrolysis of the PVA (99.8%), this represents the molar percentage of repetitive units with hydroxyl groups within the totality of repetitive units of the polymer chain, which indicates that the amount of acetate groups present in the polymer structure (hydrophobic zones) are very small in comparison with the number of alcohol groups (hydrophilic zones), which due to their polarity present a greater affinity with water, thus facilitating an uptake of water [16].
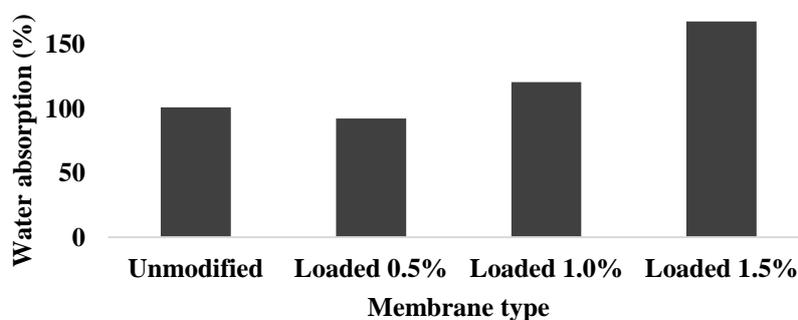

Fig. 2: Water uptake for each membrane.

The water uptake increases with increasing the Va_2O_5 load, due to the Va_2O_5 has a laminar orthorhombic structure composed of pyramids which are connected by faces, corners and edges, increasing the interaction between Va_2O_5 and the polymer network, allowing to modify properties molecular, structural, among others [18].

3.2 Ion exchange capacity

The ion exchange capacity is a fundamental characteristic on the selectivity of ions in a polymeric electrolyte, in this case the selectivity for the transport of cations in an aqueous medium. In Fig. 3 it is observed that the membranes maintain a behavior

similar to that obtained in the water absorption test since when the capacity of water absorption increases the ionic conductivity also does [19], because water provides the appropriate medium for the two main proton transfer mechanisms known as Grotthuss and vehicular [20].
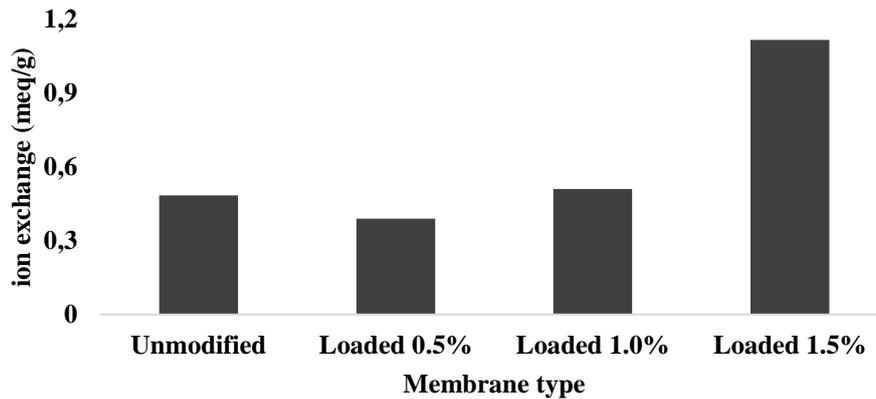

Fig. 3: Ion exchange capacity for each membrane

The results obtained agree with what was reported by a previous study [21] where the addition of Va_2O_5 favored the ion exchange as the load was increased. In addition, the ion exchange of 1.1 meq/g belonging to the membrane loaded at 1.5% exceeds by 8.8% the ion exchange present in the commercial membrane of Nafion 117 [22].

3.3 Mechanical tests

Table 1 indicates that the addition of vanadium pentoxide load was favorable to improve the mechanical properties compared to the unmodified membrane, maintaining the trend in the Young's modulus, due to the good dispersion of the charge particles in the polymer network, which makes the membrane more homogeneous and reduces the pore size in the structure formed [13].

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

Membrana type	Maximum effort (MPa)	Maximum deformation (%)	Young's modulus (MPa)
Unmodified	21.7	105.8	122.9
Loaded 0.5%	35.9	218.9	135.4
Loaded 1.0%	27.6	122.6	160.4
Loaded 1.5%	30.6	145.8	189.6

However, when analyzing the behavior of only the charged membranes, it can be seen that when increasing the load percentage, the stress and strain properties were reduced, since the optimum load limit was exceeded and when there was an excess

the load particles were not distribute evenly over the membrane facilitating mechanical rupture [21]. The mechanical properties obtained agree with other researches, obtaining PVA films loaded with reduced graphene oxide, increasing the tensile strength from 26.6 MPa to 45.6 MPa, and the Young's modulus from 144 MPa to 162 MPa [23], in the same way with Silica [24]. In addition, the results have values similar to those of the commercial membrane Nafion 117, which has tensile strength of 30.3 MPa and Young's modulus of 174.8 MPa [22].

3.4 Analysis FTIR

The infrared spectra obtained for each membrane are shown in Fig. 4. Taking into account the chemical structure of the PVA a broad peak around 3300 cm^{-1} corresponding to the OH hydroxyl bond is observed [25], a peak between 2920 cm^{-1} and 2840 cm^{-1} indicator of the symmetric and antisymmetric vibration of the CH bond [26], and the signal representative to the symmetric vibration of the CH$_2$ group is found at the peak of 1419 cm^{-1} [27]. In addition, the linkage of the formyl group -CHO given by the formaldehyde provided by the crosslinking agent in 1740 cm^{-1} and 1720 cm^{-1} is observed [14].

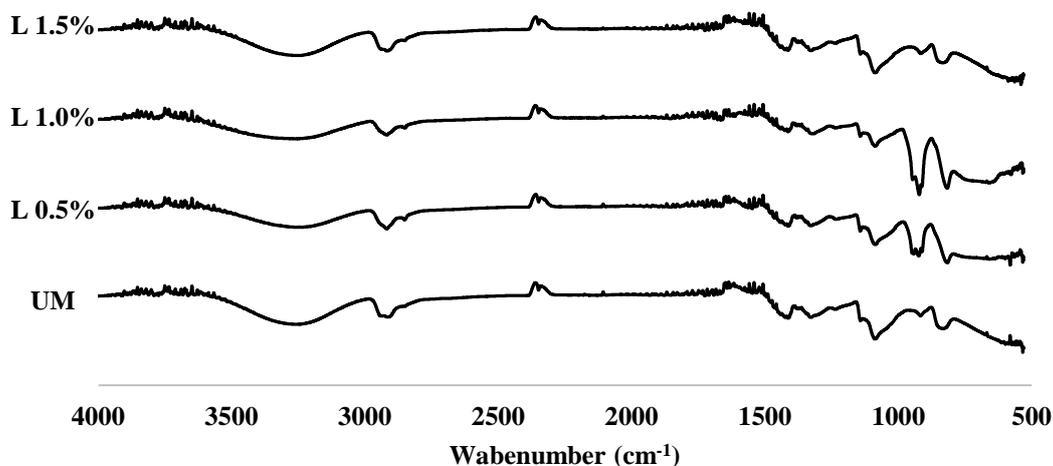

Fig. 4: Infrared spectra of the unmodified membrane, loaded 0.5%, loaded 1.0% and loaded1.5%.

The infrared spectrum of the charged membranes does not show any type of displacement in the bands of the OH or C-OH bonds of the polyvinyl alcohol with respect to the unmodified membrane, so it can be assumed that there is no hydrogen bonding interaction between the vanadium pentoxide and the polymeric matrix [28], however, the presence of Va$_2$O$_5$ in the three charged membranes is evidenced by means of the signal belonging to the vibration of the V=O bond located at 1018 cm^{-1} [29] and the asymmetric stretching of the V-O-V link located at 760 cm^{-1} [30].

4. Conclusions

In this work, the characterization of the proton exchange membranes prepared from the polyvinyl alcohol copolymer (PVA) was carried out and modified with Va_2O_5 as an inorganic filler. The ion exchange and water uptake capacity tests show better results for the membrane with higher load (1.5%); while, membrane loaded with 0.5% shows more favorable mechanical properties, and on the other hand, the FTIR tests corroborated the presence of Va_2O_5 in the polymer matrix. In general, the addition of Va_2O_5 improved the properties of the membrane and presented values similar to those of the commercial membrane Nafion 117. The previous results indicate that the prepared membranes have a high potential for their applications as electrolyte of proton exchange in fuel cells.

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