

Effect of V₂O₅ on the Proton Exchange Membrane Synthesized from Styrene - Acrylic Ester for Application in Fuel Cells

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Abstract

Proton exchange membranes were synthesized from the copolymer of styrene-acrylic ester which was loaded (% w/w) with inorganic charge of vanadium pentoxide (V₂O₅) in amounts of 2% and 4% to evaluate its application as an electrolyte in a proton exchange membrane fuel cells. The physicochemical and mechanical properties were characterized. The results show that the addition of vanadium pentoxide was favorable for the water retention test due to the hydrophilic character of the load, improving this property until 75% for load percentage of 4%. Oxidative stability and mechanical properties were also improved with the addition of load since due to the difference in pore size it became a ceramic filler restricting the mobility within the polymer matrix, however the ion exchange capacity was affected by this same reason, therefore it is necessary to improve this last property for possible use in a fuel cell.

Keywords: Styrene - acrylic ester, vanadium pentoxide, fuel cell, load, polymer membrane

1. Introduction

The dependence of fossil fuels for the obtaining of electrical energy has caused a great environmental imbalance, increasing the generation of greenhouse gases and at the same time progressively raising the average temperature of the planet [1]. It is estimated that the reserves of oil and natural gas supply for 40 more years [2],

this is the reason why for several decades new methods for the generation of sustainable energy and friendly to the environment have been developed, within this group are the proton exchange membrane fuel cells, which present high performance and eliminate the generation of pollutant gases such as SO₂ and NO_x [3]. Currently, polymer membranes are marketed that are still in development, they are expensive and have a short lifespan, some also have faults when operating at high temperatures, due to this it is necessary to develop electrolytes with new polymers or polymer combinations that allow to reach appropriate products and a better cost-benefit than the membranes available today. It has been shown that modification of the base polymer by adding an inorganic filler tends to improve the stability, water retention and mechanical properties of the membrane.

In the present work, a polymeric membrane made from the styrene - acrylic ester resin was synthesized, which was modified by adding vanadium pentoxide in different proportions to evaluate its effect on the physicochemical and mechanical properties of the membrane.

2. Materials and Methodology

2.1 Materials

A resin of the copolymer styrene – acrylic ester distributed by the company RECOL, under the name of RECOL® CRYL was used to develop this research. Vanadium pentoxide (V₂O₅), hydrochloric acid, sodium chloride, sodium hydroxide and hydrogen peroxide were also used, as well as distilled water as solvent for the preparation and characterization of the membranes.

2.2 Methodology

An unmodified membrane was prepared and two other were loaded with vanadium pentoxide (% w/w) at 2% and 4%. The unmodified membrane was obtained by dissolving 10 g of the styrene - acrylic ester copolymer in 100 mL of distilled water, this solution was subjected to stirring for 30 minutes for the correct dispersion of the polymeric material. The membrane loaded at 2% was obtained by dissolving 0.204 g of vanadium pentoxide in 100 ml of distilled water, stirring for 30 minutes and then 10 g of the copolymer was added maintaining the agitation for 30 more minutes. A procedure similar to that described above was repeated but this time increasing the amount of vanadium pentoxide to 0.417 g which represents the percentage of load of 4%. The two types of solutions prepared (unmodified and loaded) were transferred to Petri dishes, adding 25 mL of solution in each one of them; subsequently said containers were placed on a level surface and left there for 7 days, to allow complete evaporation of the solvent.

2.3 Characterization of the membranes

The water absorption was obtained taking samples from each type of membrane

with an area of 2 cm x 2 cm, the samples were initially weighed (W_s), then immersed for 24 hours in a container with distilled water at room temperature; after this time they were removed and the surface water was deleted with absorbent paper, calculating the wet weight of the sample (W_h). The percentage of water retention was calculated with the following equation [4].

$$\text{Absorbed water (\%)} = \left(\frac{W_h - W_s}{W_s} \right) \times 100 \quad (1)$$

The ion exchange capacity of the membranes was determined taking samples of the different types of membranes made from 2 cm x 2 cm area which were immersed in 1 M HCl solution for 24 hours to take it to the protonic form, after which time they were removed and washed with abundant distilled water to remove the absorbed acid. Subsequently the membranes were placed in 0.1 M NaCl solution for 24 hours, then they were removed using a sterile clamp and the solution was titrated with 0.01 M NaOH. The ion exchange capacity (IEC) was calculated by the following equation [5].

$$\text{IEC (meq/g)} = \left(\frac{V_{NaOH} * [NaOH]}{m} \right) \quad (2)$$

where V_{NaOH} is the volume (L) of NaOH used in the titration, $[NaOH]$ is the concentration (M) of NaOH and m the mass (g) of the dry membrane. The oxidative stability was determined immersing membrane samples of 2 cm x 2 cm in a solution of hydrogen peroxide for 8 days. The tolerance of the membranes to H_2O_2 is obtained by the following equation.

$$\text{Tolerance to } H_2O_2 \text{ (\%)} = \left(\frac{W_{H_2O_2} - W_s}{W_s} \right) \times 100 \quad (3)$$

where $W_{H_2O_2}$ is the weight of the membrane after immersion in at different concentrations for different times and W_s is the weight of the dry membrane.

An analysis of the mechanical properties of the membranes, as tensile strength, resistance to deformation and Young's modulus was performed using the test equipment EZ-S Universal Shimadzu at a constant speed of 250 mm/min. Finally, infrared spectroscopy was applied to investigate the interaction between the load and the polymer matrix. For this, a Nicolet 6700 Fourier transform spectrophotometer was used, obtaining the infrared spectrum in the range of lengths of wave between 4000 cm^{-1} and 500 cm^{-1}

3. Results and discussion

Fig. 1 shows the 3 types of membranes synthesized, each characterized by water

absorption, ion exchange capacity, oxidative stability, FTIR analysis and mechanical tests.



Fig. 1: Prepared membranes: a) Unmodified (UM), b) Loaded 2% (L 2%), c) Loaded 4% (L 4%)

3.1 Water absorption capacity

In Fig. 2a it is observed that the unmodified membrane showed a low percentage of water absorption of 8.6%, due to the hydrophobic nature of the resin, so it is frequently used as a waterproofing auxiliary, a characteristic attributed by the type of material and the amount of solids present (50% p / p) [6]. There is an increase in water retention (14%) for the membrane loaded at 2% but then decreases (9.3%) by increasing the amount of load up to 4%, this is due to the addition of inorganic materials in the membranes, that produce high water retention only if the particle size of material matches the pore size of the membrane. In the membrane loaded at 4%, an opposite effect occurs due to excess load, which affects its performance, since by not fitting into the polymer network, vanadium pentoxide becomes clearly a ceramic filler, which reduces the volume free of the membrane and decreases its swelling capacity [7].

3.2 Ion exchange capacity

The ion exchange capacity is deeply linked to the water retention capacity of the membrane, due to the main methods of proton migration that occur in the polymer membranes, which are the Grotthuss mechanism and the vehicular mechanism, for both cases water uptake is essential for proper transport of protons [8].

In Fig. 2b it is observed that the values obtained for the loaded membranes were lower than the result for the unmodified membrane. A greater ion exchange would be expected for this type of membranes taking into account the hydrophilic naturalness of vanadium pentoxide [9], but it can be deduced that the loading addition was unfavorable due to the expressed considerations regarding the pore size of the load and its performance as a possible ceramic filling.

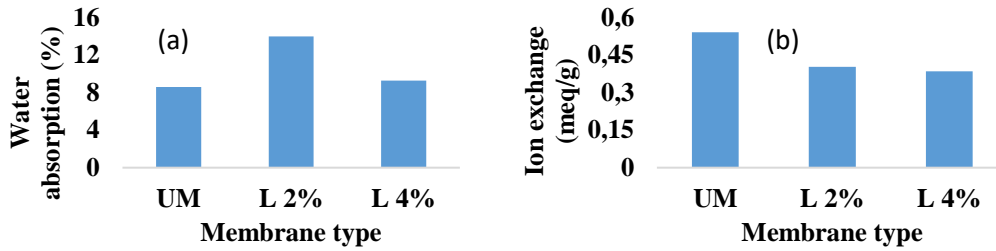


Fig. 2. a) Absorption of water for each membrane. b) Ion exchange capacity for each membrane. UM: unmodified, L: loaded.

3.3 Oxidative stability

Chemical degradation can occur either at the anode or at the cathode mainly by the formation of radicals $HO\cdot$ or $HOO\cdot$, which can attack the main chain of the polymer that forms the membrane during operation in a fuel cell.

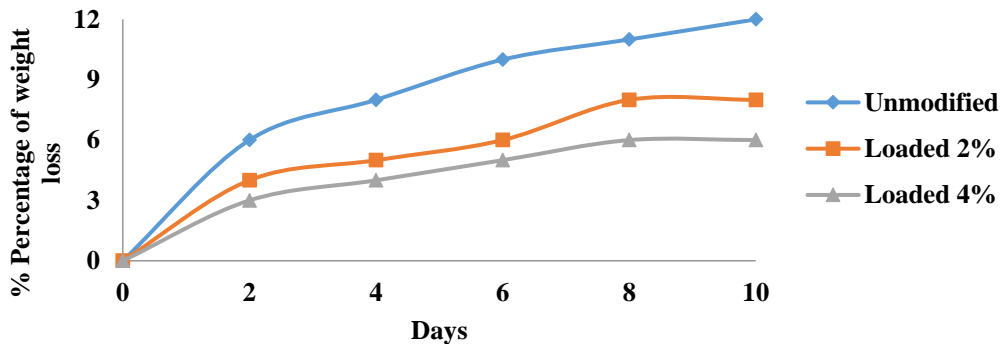


Fig. 3: Oxidative stability for each membrane.

In Fig. 3 it can be seen that the loaded membranes have a lower percentage of weight loss than the unmodified membrane, which suggests that the addition of vanadium pentoxide slightly retards the oxidative process in the proton exchange membranes, possibly because V_2O_5 acts as a ceramic filler in the internal channels of the membrane, restricting the diffusive movement of free radicals within the polymer and therefore increasing the stability of the membrane as the percentage of load increases [10].

3.4 FTIR analysis

Fig. 4 shows the infrared spectrum for each type of membrane synthesized. The characteristic vibration is observed for the bonds present in the styrene-acrylic ester resin, such as the CH bond around 3000 cm^{-1} , the C=C bond of the aromatic ring present between $1558\text{--}1500\text{ cm}^{-1}$, the carbonyl group (C=O) around 1732 cm^{-1} , the vibrations of the CH bond of the CH_2 group are observed between $1250\text{--}1500\text{ cm}^{-1}$

[11] and the vibration in 719 cm^{-1} characteristic of the styrene block present in the copolymer.

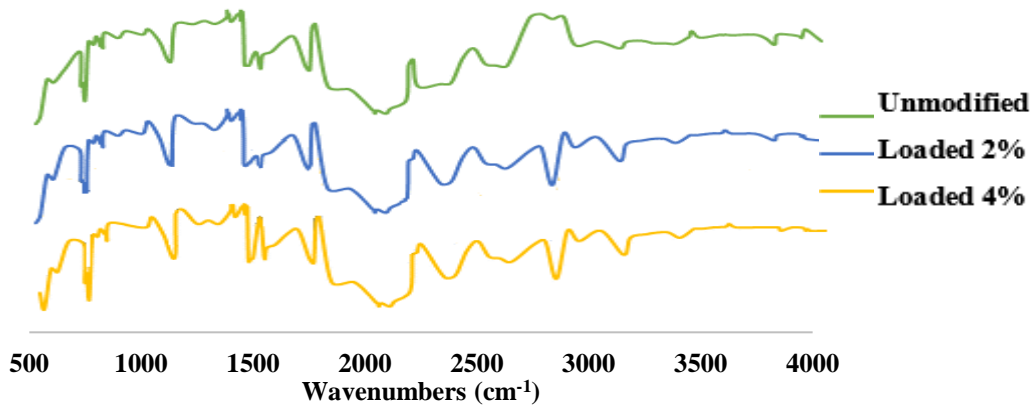


Fig. 4: Infrared spectrum for each membrane

In the charged membranes, a signal is observed in 2800 cm^{-1} which suggests the presence of the inorganic charge, showing that the percentages of vanadium pentoxide were sufficient to cause a change in the structure of the polymer, with respect to the unmodified membrane [8].

3.5 Mechanical test

The data obtained for the tests are shown in Table 1, which summarizes the mechanical properties of tensile strength, maximum elongation and Young's modulus.

Table 1. Results of the mechanical test.

Membrane type	Breaking force (N)	Maximum elongation strength (N)	Young's module (N/mm ²)
Unmodified	24,1	27,7	1,7
Loaded 2%	33,6	35,9	3,9
Loaded 4%	38,8	38,9	4,3

The addition of vanadium pentoxide improved the characteristics of the unmodified membrane as the percentage of load increased, this is due to the fact that the ceramic fillers are grouped and embedded in the existing channels between the polymer chains, thus restricting the chain mobility, which causes the increased mechanical strength of the modified copolymer [12].

4. Conclusions

In the present research project, membranes were synthesized from the styrene-acrylic ester copolymer and modified by adding vanadium pentoxide (V₂O₅) as an inorganic filler, for its application as an electrolyte in fuel cells. The FTIR analysis showed the bonds that indicates the modification of the resin given by the load. The load addition was favorable for the water absorption test due to the hydrophilic character of V₂O₅, which, not having the adequate particle size, became a ceramic filler, also enhancing the mechanical tests and the oxidizing stability of the membrane, however, the exchange capacity was affected, so it is still necessary to improve this property for possible use inside a fuel cell.

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