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Synthesis of proton Exchange membranes from a blend of copolymer Vinyl Acetate-Ester Acrylic and Natural Latex loaded with vanadium pentoxide

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Abstract : Proton exchange membranes were synthetized from vinyl acetate – acrylic ester and natural latex, and modified with different amount of vanadium pentoxide (V_2O_5). It was evaluated the membrane characteristics such aswater uptake, ionic exchange capacity, oxidative stability and mechanicals properties, the membrane without loaded (0%) obtained the highest value of water uptake (91,2%). While,the addition of vanadium pentoxide improvement the ionic exchange capacity from 0.23 to 0.722 meq/g, however, the physicomechanical properties of the membrane decrease, accelerating the oxidative capacity of the same. In the FTIR analysis were found the different functional groups corresponding to each prepared membranes.
Keywords: Natural latex, vinyl acetate, water uptake, ionic Exchange, vanadium pentoxide.

1. Introduction

Fuel cells are a promising alternative for the solution of energy and environmental problems by using of the fossil fuels such as the petroleum or coal the main precursors of energies of the world but its use has increased the CO_2 emissions in the last years[1]. These devices are able to convert chemical energy to electrical energy[2-3]using a renewable as source, this helps to reduce the environmental problems related to the combustion[3]. The membrane electrode assembly (MEA)is the core of the fuel cell where the water formation reaction occurs from hydrogen and oxygen. The hydrogen is considered a clean source energy[4]even more than other alternative energies[5], due to this many research have developed the hydrogen synthesis by photoelectrolysis of the water[6-11]. Energy from wind and solar are also considered clean energy [11-14].

In the last years have been developed the synthesis of proton Exchange membranes for use in the MEA assembly in a fuel cell, from polymers such as SEBS[15-16]vinyl acetate Esteracrylic[17], natural latex[18], among others, these have been modified with sulfonation method and the addition of loads such as TiO_2 and vanadium pentoxide, to improve the physicochemical properties and to compete in the market with used currently made with Nafion®.

Recently, it wasd eveloped the synthesis of proton Exchange membranes from styrene – acrylic ester copolymer, modified with sulfonation method and loaded with vanadium pentoxide, where favorable results were obtained [19]. This research is made the synthesis of the proton Exchange membrane from latex natural and PVA, modified with inorganic load at different concentrations and characterized.

2. Method and material

2.1. Materials

Natural latex by Ladecol S.A. and vinyl acetate–acrylic ester (P.V.A.) by Recol®, were used for the synthesis of membranes, to load the membranes was used vanadium pentoxideanddichloromethane, sulfuric acid, anhydride acetic and ethanol were used for sulfonation method and toluene for dissolution of polymer.

2.2. Synthesis of membranes

Lamination method was used for the preparation of three type of membranes: first one solution at 10% W/V is prepared using a ratio 1:1 of natural latex and PVA in water, this solution is shaken during 2 hours to obtained a homogenous mixture, then 25 ml of the solution are vertedin a plate and allowed to dry at room temperature, to obtain a membrane.

For the addition of the load is added different amounts of vanadium pentoxide corresponding to 2 and 4% W/W according to polymer mixture used previously, then is shaken during 1 hour to dissolve the load, finally is dried in the same way.

2.3. Characterization

For determining the water uptake, 1cm^2 samples of each membranes were dried in a vacuum oven at 70°C during an hour to remove the humidity excess, immediately were weighed and submerged in distilled water during 24 hours, after , samples were weighed but first water from the surface is removing[20]. To calculate the water uptake next equation is used:

$$\%\ water\ uptake = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) x\ 100 \qquad (1)$$

Where W_{wet} and W_{dry} are weight wet and weight dry of the sample.

For determining the ion exchange capacity characterization, the samples were weighed and protonated in a 1M chlorohydric acid solution during 24 hours, then, samples were washed and submerged in a 1M NaCl solution during 24 hours, to generate the ion exchange, and finally, the solution is tittered with sodium hydroxide 0.1 M[21]. Ion exchange capacity is calculated by:

$$IEC\ (mequiv/g) = \frac{Volume\ Of\ NaOH\ x\ [NaOH]}{weigh\ of\ sample} \qquad (2)$$

Functional groups were determined with infrared spectra, while mechanicals properties were measured by the universal testing machine manufactured by EZ-S Shimazu.

3. Results and discussion

Figure 1 shows membranes synthetized, the loaded 0, 2 y 4% W/W where the increase of the load quantity increases the intensity of the color.

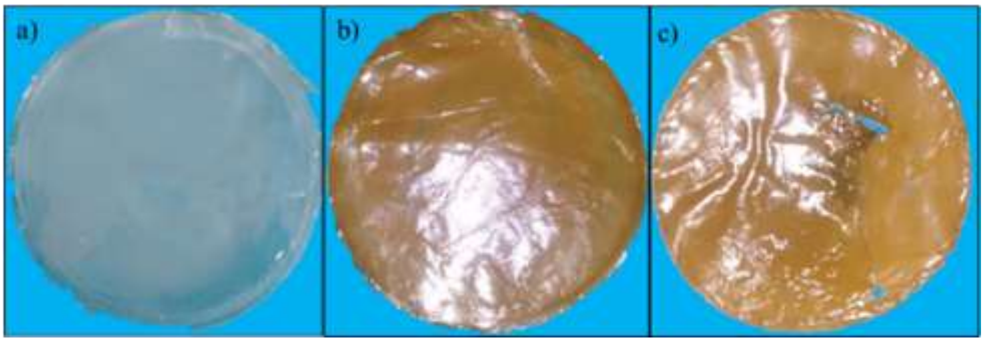

Figure 1. a) Loaded 0%, b) loaded 2%, c) loaded 4%

3.1. Water Uptake

Water uptake is one of the requirements more important of the proton exchange membranes due to is directly related to ionic conductivity and its utility in fuel cells[22]. Figure 2 shows a high water uptake value in each samples, it can see that 91.2% is the maximum water uptake value corresponding to L0%, 75% for L2% and 61,4% for L4%.

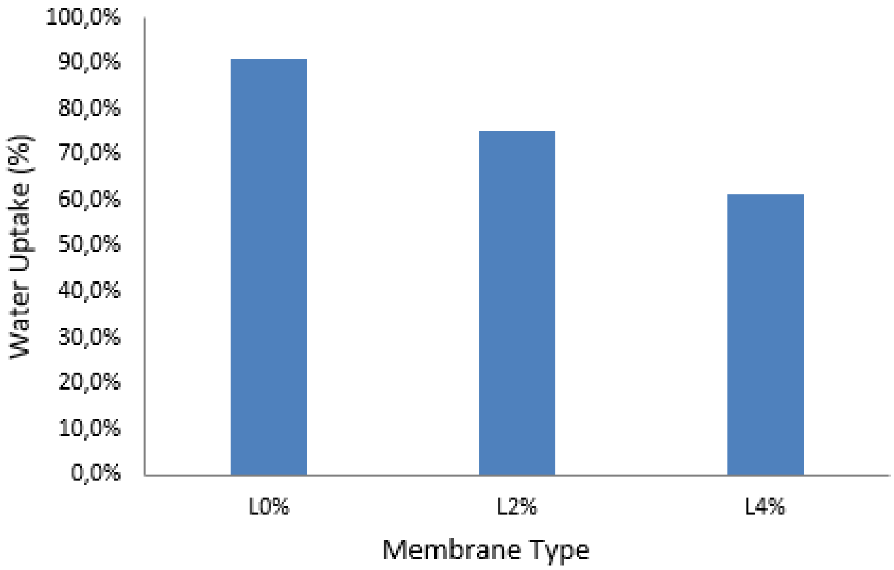

Figure 2. Water Uptake of membranes

Vinyl acetate increases water uptake due to is a highly hydrophilic material [17],by other side it would be expected that the presence of vanadium pentoxide also increase the water uptake since it is an inorganic material and is highly oxidative [18], however this not occur because the membrane is composed by three types of different polymers, including the acrylic ester that provides hydrophobicity to the membrane and agglomerating and block the V_2O_5particles, avoids that interact with the water and the natural latex and vinyl acetate chains oxidized[22].

3.2. Ion Exchange Capacity

Figure 3 shows ionic exchange capacity where this increases with presence of vanadium pentoxide. Vanadium pentoxide has a high oxidative power that accelerates the ion exchange in the membrane, due to the formation of bond type V–OH on the surface increasing the number of sites available for ion exchange[23].However, when the load increases, then ion exchange capacity decreases due to the saturation that this causes in the surface of the membrane, in the same way as reported in [18]. This values compared to the Nafion 115 and Nafion 117 membranes [24-25]are no far taking into account the addition of sulfonic groups.

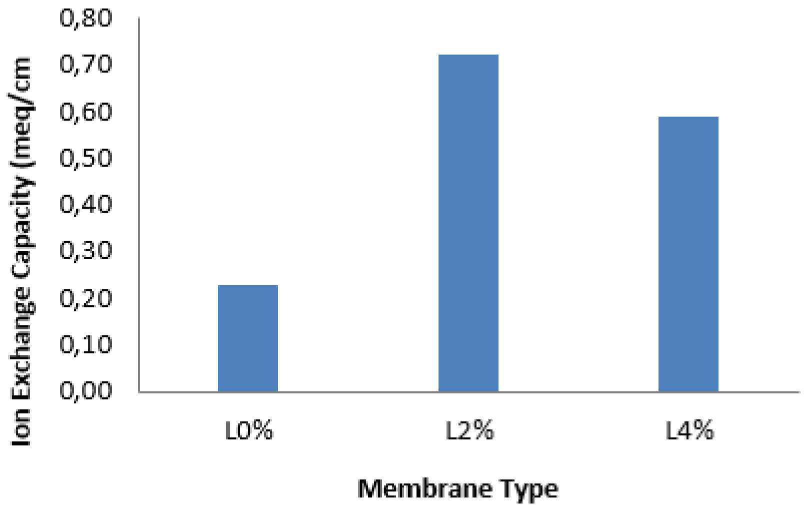

Figure 3. Ion Exchange capacity

3.3. Oxidative Stability

Figure 4 shows the mass loss of each membrane by the immersion in a H_2O_2 solution during 7 days, this characterization is known as oxidative stability. The loss weight increases with increasing the vanadium pentoxide quantity.

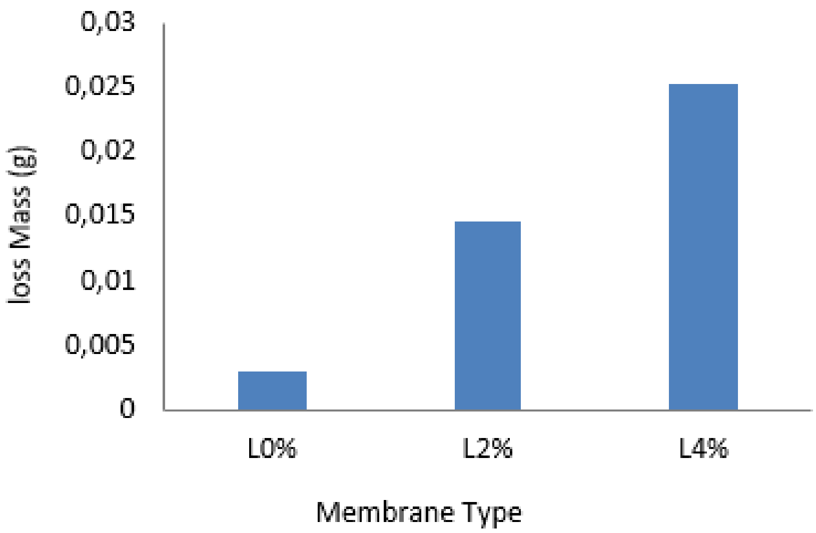

Figure 4. Oxidative Stability

As already mentioned, the oxidation tendency of vanadium is high, during immersionin, this degrades the samples, in addition over time the vanadium pentoxide that remains in the surface of the membranes is detach, therefore causes greater weight loss.

3.4. FTIR spectra

Figure 5 shows the spectra performed from FTIR analysis for each synthetized membrane. In each of the spectra can be observed in the region between 2927-2960 cm^{-1} the presence of a peak representing a small vibration of the hydrogen carbon bond (C-H) corresponding to the Acetate Vinyl present in PVA-EA[26]. In the range of 1730-1750 cm^{-1} there is a peak corresponding to the stretching of the C=O bond for the acrylic ester[27].

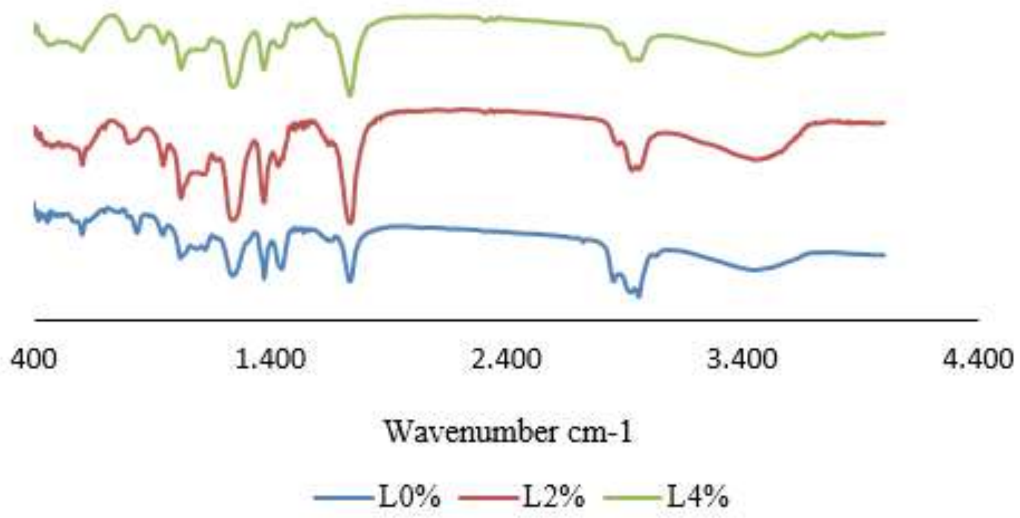

Figure 5. FTIR spectra of prepared membranes

For natural latex a peak of 1651 cm^{-1} in the spectra of L0% and L2%, and 1647 cm^{-1} for L4%, this is corresponding to the tension of the carbon-carbon double bond of isoprene[28], for L2% and L4% peak is present in 1024 cm^{-1}, which is attributed to the vibrations of the V=O bond of vanadium pentoxide[29].

3.5. Mechanical properties

Mechanical properties of synthetized membranes are shown in the table 1, where is observed that the tension presents a maximum value in the loaded 2% membrane, while the maximum displacement has a minimum value in the same type of membrane, however, is observed that the addition of the load in greater proportions makes the membrane less rigid and more sensitive, since due to the moisture content of the membrane, the vanadium pentoxide oxidizes the membrane more easily[28], as observed in the stability oxidative, this permit that the membrane lose rigidity by the oxidation.

Values of tensile stretch are higher than reported by [30](2.95 N/mm^2) and[10](5,99 N/mm^2) for natural latex and PVA- EA, respectively. However for Nafion 117 membrane, values of 43,5 N/mm^2 have been reported, but still, the implementation of these membranes can be carried out in fuel cells, because membranes with lower value (8.3 N/m^2) have been tested in fuel cells [31].

Table 1. Mechanicals Properties

Sample	Tensile stretch (N/mm^2)	Displacement (mm)	Break (N)
L0%	84,7	92,1	8,5
L2%	9,9	2,3	7,9
L4%	7,9	4,3	7,0

4. Conclusions

In this research, proton exchange membranes from PVA-EA and natural latex were synthetized. Loaded 2% membranes with V_2O_5 have important characteristics to be implemented in fuel cells such as electrolyte, although unmodified membranes obtained a higher water uptake value, mechanical stability decreased. By other hand, ion exchange capacity is an important characteristic in proton exchange membranes and it was obtained that the membranes with loaded 2% obtained the highest value, the addition of small quantities of an inorganic load helps to improve the characteristics of a proton exchange membrane for its use in fuel cells.

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