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# Synthesis of a Proton Exchange Membrane from Natural Latex Modified with Vanadium Pentoxide for Application in a Fuel Cell

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Abstract : Proton Exchange membranes were synthetized using natural latex of rubber trees from Cartagena, Bolívar. Natural latex was modified by the addition of an inorganic load  $(V_2O_5)$  at different amounts (2, 4 and 6%), to improve the proton exchange and physicochemical properties. It was evaluated the ionic Exchange capacity, the water uptake and the oxidative stability for each sample. Membranes loaded with 6% V<sub>2</sub>O<sub>5</sub> showed highest water uptake (values 20,34%), and highest mechanical properties. However, ionic exchange capacity of membrane loaded with 4% showed highest values, due to a saturation in membranes. These characteristics attribute high potential for applications in a fuel cell.

Keywords : Fuel cell, membrane, Natural latex, load, vanadium pentoxide.

# 1. Introduction

Technological advances have grown exponentially over time, proportionally to the demand of the human consumerism, due to that nowadays any transaction or activity require to implement the technology, so it's known that there is technology, is necessary use energy, which has generated to the massive exploitation of the petroleum and other fossils oils, generating the possible extinction of the same, but the demand of energy continues day to day. It is necessary to implement alternative energies to not stop technological growth<sup>1-3</sup>. That's why is doing many researches about alternative energies, which not only are durable but also be friendly to the environment.

Fuel cells are part of this possible solution; these devices transform the chemical energy to electrical energy, using the hydrogen as fuel, generating water from this reaction<sup>4</sup>. There are many types of fuel cell such as the PEM type, (proton exchange membrane), these types of fuel cells generate higher amount of current than others<sup>5</sup>.

Actually, Nafion membranes are the most used due to high proton conductivity and a high mechanical stability; however, this type of membrane has high cost<sup>5</sup>, and this reason have motivated the developed of many synthetize of polymeric membranes using different polymer to be used in fuel cells<sup>3-11</sup>. In this research, natural latex is used as alternative to develop polymeric membranes, it was loaded with vanadium pentoxide and characterized by different methods to define its use in fuel cells.

#### 2. Method and Materials

#### 2.1. Materials

The materials used are: natural latex from de tree *brasilis* ,manufactured by Ladecol, Vanadium oxide, methylene chloride, toluene, ethyl alcohol, hydrogen peroxide, hydrochloric acid, sulfuric acid, acetic anhydride. Sodium chloride, sodium hydroxide.

#### 2.2. Methodology

Initially, membranes without loaded were prepared by a mixture of 30% w/v of latex and distilled water, and the solution was shaking for half hour, then twas shed in a petri dish of 25ml and it was hoped the solvent vanished for obtaining the membrane laminated. Loaded membranes were prepared by adding different concentrations of vanadium (2, 4 y 6%) pentoxide to the solution and shaking for an hour.

#### 2.3. Characterization

Water uptake in the membrane was determined by immersion for 24 hours in a container with distilled water; then excess water was removed with a filter paper, the wet weight of the sample was calculated ( $W_h$ ). Immediately the membrane was dried at 75 ° C for a time of 2 h to determine the weight of the dried sample (Ws). The percentage of water retention was calculated by the following expression<sup>12</sup>.

% Water Uptake = 
$$\left(\frac{W_{h} - W_{s}}{W_{s}}\right) * 100$$
 (1)

Proton exchange membranes were characterized by ion exchange capacity that is defined as the number of millimoles of  $H^+$  per unit mass of the dry membrane. This process is carried out by immersion in a solution of HCl for 24 hours. Then, the membrane is immerse in 50 ml of 1M NaCl for another 24 hours to produce the ion exchange between the protons of the membrane and sodium ions. The solution was titrated with NaOH to the equivalence point<sup>13</sup>. The percentage of water uptake is calculated by the following equation<sup>14</sup>

$$IonExchangeCapacity = \left(\frac{V_{NaOH} * [NaOH]}{m}\right)$$
(2)

where,  $V_{NaOH}$  is the volume of NaOH used in the titration, [NaOH] is the concentration of Na+ and m is the mass of dry membrane.

Infrared spectroscopy (FTIR) was carried out by the method of the Fourier transform (FTIR) to determine the interaction of sulfonic groups attached to the membrane through sulfonation using the spectrophotometer Nicolet 6700<sup>14</sup>.

#### 3. Results and Discussion

Figure 1 shows four type of loaded membranes were prepared (0, 2, 4 and 6% w/w), each membrane was characterized by water uptake, ion exchange capacity, oxidative stability and mechanical properties.



Figure 1. Prepared Membranes: a) Loaded 0%, b) Loaded 2%, C) Loaded 4%, d) Loaded 6%

#### 3.1. Water uptake

Water uptake was determined by the methodology previously mentioned, water uptake is important in the determination of performance of the proton exchange membrane, due to the water is necessary as a mobile phase to facilitate the protonic conductivity; however, the water absorbed also affects the mechanical properties in the membrane<sup>15</sup>

Figure 2 shows that the water uptake increases with increasing the load of vanadium pentoxide. Membrane without load shows a low value of water uptake due to the solids of the polymer, which tend to form films that sealing the pores of the membrane<sup>16</sup>. The addition of inorganic to the membrane increased the water uptake from 11,27% to 20,34 %, due to the oxidative power of the vanadium<sup>17</sup>, what produced that the membrane suffered a swelling producing free spaces to the introduction of the water molecules.



Figure 2. Water uptake of prepared membranes

#### 3.2. Ion Exchange Capacity

Ion exchange capacity is the number of  $H^+$  ions replaceable per unit of mass of the dried membrane, this is one of the characteristic more important in the proton exchange membranes, due to that provides an indication about the acids groups that have  $H^{+18}$ . In Figure 3 is observed that the ion exchange capacity increases in accordance with the addition of the load to the membranes, however it is observed that the membrane loaded with 6% decreases the ionic exchange value.



Figure 3. Ion Exchange Capacity of prepared membranes

The high oxidation potential of  $V_2O_5$  oxidizes the water molecules present in the membrane, groups of the VOH in the surface of the particles are produced and the water uptake in the membrane is caused, and the increase of available sites to ion exchange<sup>19,20</sup>. However, in the membrane loaded with 6% is observed a reduction in the ionic exchange, what it can be attributed to a lock carried out by the  $V_2O_5$  that interrupts the movement of the ions due to a glut of the same ions<sup>21</sup>.

#### 3.3. Oxidative Stability

Samples of each type were submerged in a  $H_2O_2$  solution to determine its stability oxidative, the samples were weighed every 24 hours for 7 days. First day should have a swelling in the membranes, by the absorption of the aqueous part of hydrogen peroxide, however this was controlled due to samples were dried at  $80^{\circ}$ C in the oven by 1 hour to retire the water excess.

The figure 4 shows that the membrane without load has highest stability. The presence of vanadium in the membrane provides available sites to the oxygen absorption and cause in the membrane an oxidation more effectively for degradation<sup>22</sup>.



Figure 4. Water loss of prepared membranes in different vanadium pentoxide load

#### 3.4. Fourier Transformed Infrared (FTIR)

This method was used to characterize chemically the synthetized membranes; it was used Nicolet IR equipment to analyze the functional groups. Figure 5 shows the different incidences and spectra for each membrane. Latex or rubber natural is made exclusively of isoprene polymer, in 1600-1670 cm<sup>-1</sup> (B) range each sample shows peaks corresponding to the tension of C=C bond and the tension out the plane of C=CH bond<sup>23</sup>.

In 2700 – 3500 cm<sup>-1</sup> (A, B) range is shown a width peak corresponding to water used in the solution of natural latex of the synthesis of the membranes. It is known that  $V_2O_5$  showed high absorption in 617 and 827 cm<sup>-1</sup>(E), associated to vibration V-O-V and O-(V)<sub>3</sub>, respectively. These signals can be observed in 708 and 822 cm<sup>-1</sup> (E, F). In addition, it is observed a peak close to 1022 cm<sup>-1</sup>(D) corresponding to stretch V=O bond<sup>24</sup>.



Figure 5. FTIR spectra of prepared membranes

### 4. Conclusions

In this research was performed the synthesis of polymeric membranes loaded with  $V_2O_5$  using natural latex obtained by the trees from Cartagena. The addition of  $V_2O_5$  increases the water uptake and ionic exchange capacity of the membrane, while, the stability of membranes decreases with increasing the  $V_2O_5$  load. The FTIR test shows peaks that indicates the presence of vanadium in the membranes prepared.

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## References

- 1. A.Realpe, J.Orozco, M.Acevedo, (2015), Windpower for hydrogen production using a spiral electrolyzer, International Journal of Applied engineering Research, 10(4), pp. 9175-15913.
- A.Realpe, D. Nuñez, I. Carbal, M. Acevedo, (2015), Preparation and characterization of titanium dioxide photoelectrodes for generation of hydrogen by photoelectrochemical wáter spliting, International Journal of Engineering and Technology, 7(2), pp. 753-759.
- 3. A.Realpe, D. Nuñez, I. Carbal, M. Acevedo, (2015), Sensitization of TiO2 photoelectrodes using copper phthalocyanine for hydrogen production, International Journal of Engineering and Technology, 7(4), pp. 1189-1193.
- 4. P. Sapkota, H. Kim, Zinc Air fuel cell, a potential candidate for alternative energy, Journal of industry and engineering chemistry.
- Hooshyari, K., M. Javanbakht, L. Naji y M. Enhessari, Nanocomposite proton exchange membranes based on Nafion containing Fe2TiO5 nanoparticles in water and alcohol environments for PEMFC, Journal of Membrane Science: 454(1), 74-81 (2014).
- 6. A. Realpe, Y. Pino, M. Acevedo, Synthesis of a Proton Exchange Membrane Obtained From SEBS Copolymer For Application In a Fuel Cell, International Journal of Applied Engineering Research, 10(6) (2015), 15905-15913.

- 7. A. Realpe, N. Mendez, M. Acevedo, (2014), "Proton Exchange Membrane from the Blend of Copolymers of Vinyl Acetate-AcrylicEster and Styrene-Acrylic Ester for Power Generation Using Fuel Cell", International Journal of Engineering and Technology, 6(5), 2435-2440.
- 8. A. Realpe, K. Romero, M. Acevedo, (2014), Síntesis de Membranas de Intercambio Protónico a Partir de Mezcla de Poliéster Insaturado yLátex Natural, para su uso en Celdas de Combustible Información tecnológica 26, pp.55-62.
- 9. A. Realpe, Y. Pino, M. Acevedo, (2015), Effect of sulfonation of SEBS copolymer on the physicomechanical properties of proton Exchange membrane, International Journal of Engineering and Technology, 7(4), pp. 1438-1442.
- A. Realpe, K. Romero, M. Acevedo, (2013), Synthesis and characterization of proton Exchange membrane from Blend of unsaturated polyester resin and natural rubber, International Journal of Engineering and Technology, 4(9), pp. 4005-4009.
- 11. A. Realpe, N. Méndez, E. Toscano, M. Acevedo, (2015), Síntesis y caracterización fisicoquímica de una membrana carga con TiO2 preparada a partir de la sulfonación de un copolímero de Ester acrílico y estireno, Información tecnológica, 26(5), pp. 97-104.
- 12. Gunduz, N. 2001, "Synthesis and Characterization of Sulfonated Polyimides as Proton Exchange Membranes for Fuel Cels", Blacksburg.
- 13. D. Gonzalez, L. Martínez 2009, "Síntesis Y caracterización de una membrana de Intercambio Aniónico con aplicación en Celdas de Combustible Alcalinas", Universidad Nacional.
- 14. S. Zaidi, Polymer sulfonation versatile route to prepare proton-conducting membrane material for advanced technologies, The Arabian Journal for Science and Engineering 28 (2003)183-194.
- 15. M. Hickner, H. Ghassemi, Y. Kim, B. Einsla, J. McGrath, 2004, "Alternative Polymer Systems for Proton Exchange Membranes (PEMs)" 4587Chem. Rev 104 (2004), 4587–461.
- Mahyuddin R. M.Z. 2001, "Durability stidies of blended natural-synthetic polymer modified mortar and ferrocement", Seven international symposium on ferrocement and reinforced cement composites, 431-439.
- 17. Palermo. V, 2012, "Síntesis y caracterización de heteropoliácidos constituyendo materiales híbridos para su aplicación como catalizadores en la oxidación ecocompatible de sulfuros", Tesis doctoral, Universidad Nacional de la Plata.
- 18. P Dimitrova, K.A Friedrich1, B Vogt, U Stimming, 2002, "Transport properties of ionomer composite membranes for direct methanol fuel cells" Journal of Electroanalytical Chemistry, 532 (2002),75-83.
- 19. Shevchenko, V., A. stryutskii y N. Klimenk, 2011, "Polymeric organic-inorganic proton-exchange membranes for fuel cells produced by the sol-gel method", Theoretical and Experimental Chemistry: 47(2), 67-91.
- 20. Realpe. A, Mendez. N, Toscano. E, Acevedo. M, 2015, "Síntesis y Caracterización Fisicoquímica de una Membrana Cargada con TiO2 Preparada a Partir de la Sulfonación de un Copolímero de Éster Acrílico y Estireno" Información Tecnológica: 26(5), 97-104.
- 21. Barbora. L, Acharya. S, Verma. A, 2009 "Synthesis and ex-situ characterization of Nafion/TiO<sub>2</sub> composite membranes for direct ethanol fuel cell" Macromol Symp, 277, 177-189.
- 22. Papa. J, Armas. N, Brito. J, Marzuca. S, de Risi. L, Rosillo. C, Guaran. N, 2007, "Deshidrogenación oxidativa de n-pentano sobre catalizadores a base de óxidos de vanadio y magnesio modificados con á-Al2O3", Revista de la Facultad de Ingeniería Universidad Central de Venezuela, 22(3), 47-58.
- 23. A. Cáceres, (2011), "Estudio de caracterización Fisicoquímica de Látex Natural proveniente de Hevea Brasiliensis por medio de termogravimetría", Universidad Industrial de Santander.
- 24. Chen. W, Qiang. L, Feng. J, Qing. Z, Yao. Q, 2004, "FTIR study of vanadium oxide nanotubes from lamellar structure", Journal of materials science, 39, 2625-2627.

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