



CHARACTERIZATION OF CHITOSAN PROTON EXCHANGE MEMBRANE

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ABSTRACT

The proton exchange membrane is a fundamental part of the fuel cell. Up to now only Nafion® from D upont® is the best membrane because of its conduction properties, so it becomes necessary to develop new materials improving its conduction, but also mechanical and absorption properties. On this work the use of a biopolymer called chitosan is proposed as a less-expensive and environmentally-friendly alternative membrane for proton exchange membrane fuel cells. The evaluation of chitosan membranes with different molecular weight was made using Nafion® 117 as control, the variables for the biopolymer were: high, medium, low and practical grade, all with sulfite groups like proton conductors from activation with H₂SO₄, this evaluation included thermal stability, proton conductivity and water absorption. Results indicate proton conductivity increases with molecular weight and thermal stability shows temperature at which the material is completely decomposed. The molecular weight difference is the energy used to break bonds, while the weight lowers the peaks decrease, it applies to all weight except for the medium which was the smallest. The water absorption was the same for the different molecular weight.

Key words: Chitosan membrane, proton conductivity, thermal stability



1. INTRODUCTION

The proton exchange membrane is an important component for the fuel cell, because it separates the reactant gases, transports the protons from anode to cathode; to complement its function the membrane needs to have high conductivity, good fuel barrier properties, high mechanical strength, thermal and chemical stability, electronically non-conducting, and low cost.

This membrane is a solid polymer electrolyte, which in presence of water, the negative ions are rigidly held within the structure, only the positive ions contained within the membrane are mobile and are free to carry positive charge through the membrane, in the polymer electrolyte membranes fuel cell, the protons are the hydrogen ions.

Nowadays, the Nafion[®] (Dupont) composed by a perfluorinated backbone with side chains that are terminated by strong acid SO_3H groups, is the best membrane but it is expensive, depends on water for conduction and is unstable at temperatures above 100°C . For that reason it is necessary to develop new materials with better properties, like chitosan.

The chitosan is a polyelectrolyte derived from chitin, supporting material for the crustaceans, insects, etc, through a deacetylation process. It's the second biopolymer most abundant in nature, only after the cellulose. It is inert, hydrophilic, and insoluble in water, alkali and organic solvents. Its solubility in dilute organic acids allows for gel formation in various configurations, membranes included. (1)

The chitosan itself doesn't have conductivity, only in an acidic medium through the protonation of the $-\text{NH}_2$ groups (1) at operation conditions in a fuel cell the membrane should be crosslinked in order to ensure physical and chemical stability in the presence of water.

2. METHODOLOGY

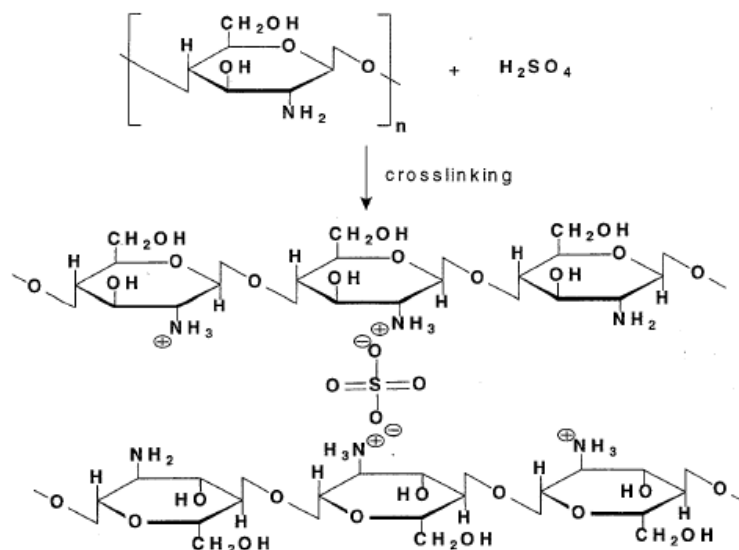
2.1 Preparation of membranes and activation

2.1.1 Nafion 117

This membrane Nafion 117[®] (N117) was supplied by Fuel Cell Store, is activated by dipping for one hour in a solution of 3%v H₂O₂ and H₂SO₄ 2M at 70°C-80°C interspersed by deionized water at the same conditions.

2.1.2 Chitosan membranes

To prepare membranes, 1 g of chitosan supplied by Sigma Aldrich, in four different molecular weight: high (CH), medium (CM), low (CL) and practical (CP) grade was diluted in 100 mL of acetic acid during 1 h approximately. The time for dissolution increases with the molecular weight, and also the time for filtration, which is the next step, finally dissolutions filtered were dried at room temperature. The neutralization, was induced with NaOH 2M for 5 minutes and then the membranes were dipped in H₂SO₄ 0.5 M for 24h, for being cross-linked and protonated, which decreases the crystallinity according to mechanism explained by Mukoma, et. al. [1] showed in the following scheme.



Scheme a) crosslinked chitosan membranes (1)

2.2 Characterization of membranes

2.2.1 Proton conductivity

In order to know the proton conductivity of the chitosan membrane and to compare it with Nafion[®] 117, the four-point-probe conductivity cell was measured with a potentiostat PAR-2273, with a cell home-made, the material of electrodes used was stainless steel, supported on Teflon[®]. The impedance spectra of membranes were obtained at open circuit potential (E_{oc}). The amplitude of the signal perturbation was 10 mV, the frequency range scanned was from 100 Hz to 1 Hz. The measurements were performed at room temperatures of interest under 100 % of relative humidity.

2.2.2 Thermal Stability

For the thermal stability TGA-DSC analysis was made by means TA Instruments SDT Q600 V20.9 Build 20 in experiment range from 24 to 400°C in a nitrogen atmosphere. It was used to know thermal decomposition of the membrane and to know the optimal temperature for membrane electrode assembly, as for Nafion 117.

The TGA, thermal gravimetric analysis, was made with a mass ranging between 5 – 15 mg of each membrane, in an alumina pan. The curve obtained shows a mass loss as a function of temperature.

For differential scanning calorimetry (DSC) characterization, the sample was weighed on a microbalance in alumina pans, scanned with the heat flow measured versus temperature in nitrogen atmosphere.

2.2.3 Water absorption

Three pieces of membranes were hydrated for 24 hours with deionized water, the mass was measured with a Mettler Toledo analytical balance, and dry in desiccators for 2 days and weighted again.

3. RESULTS

3.1. Proton conductivity

The impedance spectra of membrane are shown in figure 1 (a-d). In these figures the real and imaginary components of Nyquist diagram show the membrane resistance.

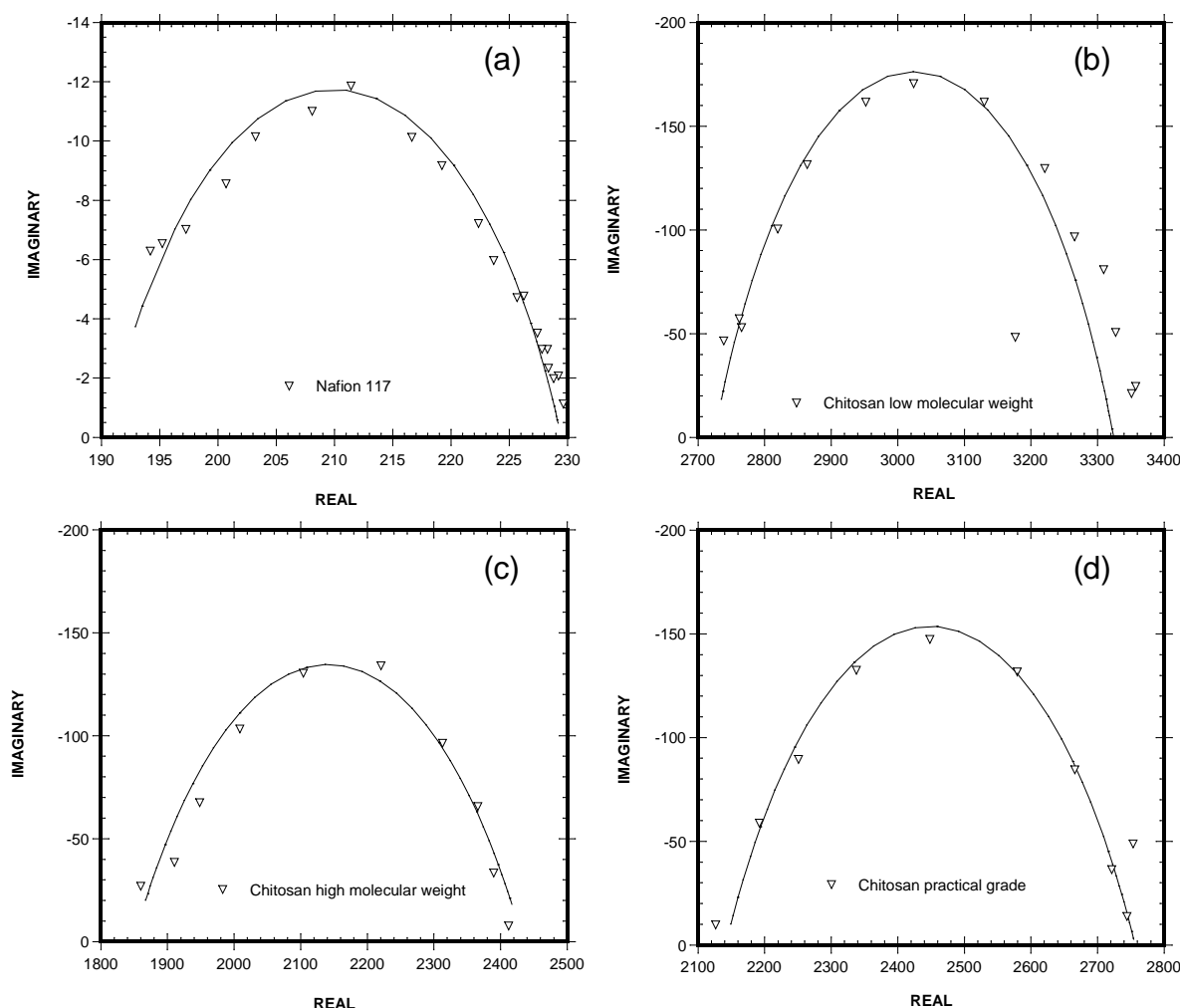


Figure 1. Nyquist spectra of membranes at 25°C and 100% of relative humidity: a) Nafion® 117, b) Chitosan low molecular weight, c) Chitosan high molecular weight and d) Chitosan practical grade.

One electric circuit was employed, figure 2. The electric circuit was used to simulate the impedance response of those spectra. Then the equivalent circuit for membranes is a resistance R_0 that accounts for the proton resistance in series with a circuit in parallel. This parallel circuit is made up of a resistance R_p that represents a polarization resistance in parallel with a constant phase element (CPE). This $R_p(\text{CPE})$ circuit is associated to inter-phase between the membrane and stainless steel electrodes.

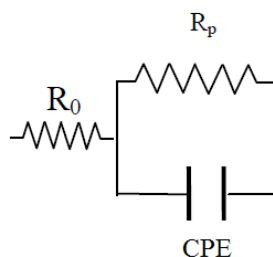


Figure 2. Equivalent circuit showing the proton resistance in series with R(CPE) circuits.

Table 1 shows the best-fit values of electrical elements in figure 2 with the experimental impedance spectra and using the Boukamp EQIVCT fitting program. The electric circuit allows a good fit ($\chi \sim 10^{-3}$ - 10^{-4}) to experimental impedance spectra.

Table 1 Best-fit values of impedance spectra of the membranes and electric circuits in fig. 2.

Sample	R_0 Ω	R_p Ω	CPE ($F/(cm^2 s^{n1-1})$)	n1
N117	205	20	3.12×10^{-5}	0.73
CL	2724	600	1.44×10^{-5}	0.67
CH	1847	584	3.7×10^{-5}	0.54
CP	2141	615	2.9×10^{-5}	0.58

Knowing the resistance R_0 from the graphics, and the various thickness and areas, the proton conductivity was calculated. The resistance, R_0 , is associated to membrane-structure, where the protons, in this case are moved between the stainless steel electrodes because of the potential difference. The proton conductivity, K , was calculated from R_0 by means of the following expression:

$$K = \frac{l}{A * R_0} \quad (1)$$

Where: K is the proton conductivity [$S cm^{-1}$], l is the length between electrodes [1 cm], A is the area [cm^2] and R_0 is the resistance [ohm]. The values of the conductivities of the membranes

are given in Table 2. In this Table the proton conductivity increases while the molecular weight increases, and it could be related with the number of functional groups in this cases the SO_4^- due to the bigger size of the molecule, and has more branches in which this groups could be bonded. The proton conductivity of the chitosan membranes differs in one order of magnitude from those for Nafion[®], and the conductivity increases with the molecular weight. This only can be seen in the high and low molecular weight, in the practical grade the cause for high conductivity could be that it isn't totally pure and the molecular weight is not defined. Also there were differences between the thicknesses, in future studies it should be controlled.

Table 2. Conductivity of the membranes obtained as a function of impedance spectroscopy.

Membrane	K [S cm ⁻¹]
N117	7.7×10^{-2}
CL	3.73×10^{-3}
CH	9.2×10^{-3}
CP	7.44×10^{-3}

3.2. Thermal Stability

In the figure 3 the (a) lines describe the loss of weight and the (b) curves area the derivative of heat flow, joining both, the behavior is similar in the four cases, despite that high molecular weight shows the largest peaks. For all the cases the first loss of weight (I) is between 40-100°C of 8 %, and is caused by water evaporation, the two peaks of DSC seen are endothermic. The second stage shows a loss of weight in a little range of temperature with peaks of bigger energy, that is the first step for degradation of the material (28% loss of weight), the second step was slower with an endothermic peak followed by an exothermic (50% loss of weight), after that, all the membrane is expected to be converted completely into carbon due to the nitrogen atmosphere during operation. By comparing results with those reported by P. Mukoma *et al.* (1) the behavior of the crosslinked chitosan is almost the same in nitrogen.

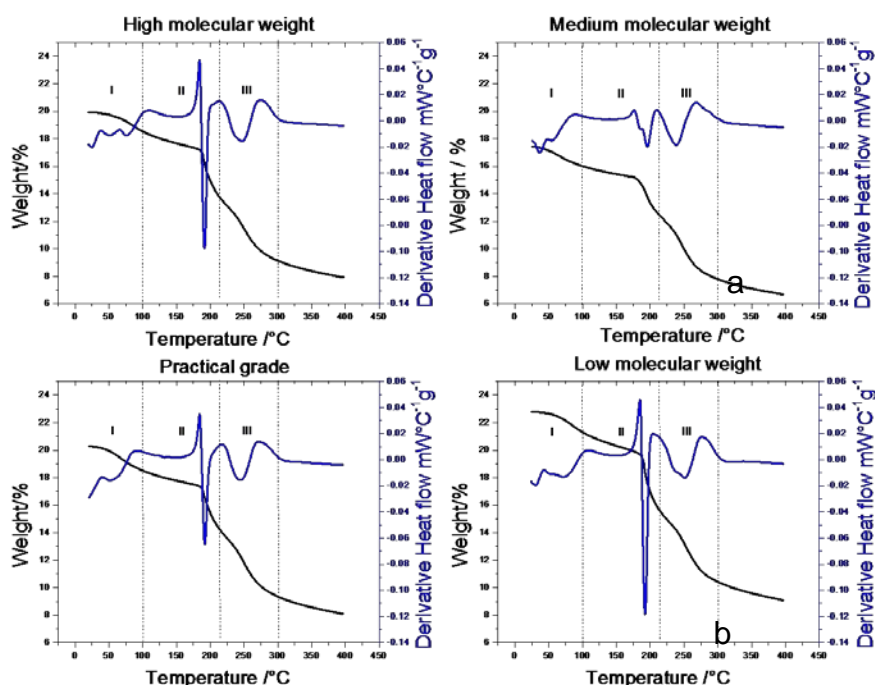


Figure 3. Compare (a) TGA- (b) DSC curves of chitosan of different molecular weight. Three peaks were showed first the evaporation of water, and the other two peaks area degradation of the chitosan in two steps.

The curves low and practical grade are very similar, in contrast the medium and high molecular weights samples present the minimum and maximum respectively in energy requirements for their transformations. So, the differences between the four molecular weights are the energy required for break bonds, but all events occur in the same range of temperatures.

3.3. Water absorption

The results obtained for the water uptake of the membranes are shown in Table 3. There is no difference in water absorption related with the molecular weight or thickness. The thickness was measured by a Mitutoyo micrometer. But with reference to Nafion®, chitosan membranes prepared showed almost 20% more water uptake. A minor deviation from real values must be taken due to the lack of micrometric control of the thickness for each sample in dried process.

Table 3. Water uptake capacity

MOLECULAR WEIGHT	%w	THICKNESS (mm)
N117*	33%	0.175
CL	51%	0.143
CH	55%	0.217
CP	54%	0.166
CM	50%	0.370

*Data from [1] Mukoma et al. with temperature water controlled at 27°C

4. CONCLUSION

The proton conductivity increases in a direct proportion to molecular weight. In reference to thermal stability, the energy to break the chemical bond in the structure, shows a first decomposition for all the molecular weight studied, with an exo and then an endo peak. Chemical analysis like FTIR should confirm exactly the chemical changes involved in each thermal event. Meanwhile, the chitosan membranes starts degradation before Nafion® [1] that is between 150-210°C, where the energy is greater as the mass loss, then, for its use in fuel cells, temperatures for electrode-membrane assemblies must be less than 140°C in order to avoid decomposition. According to the reference [1] Nafion® starts degradation between 270 and 300 °C, which is a disadvantage according to the product of Dupont®.

5. ACKNOWLEDGEMENTS

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