Effects on Nafion® 117 Membrane Using Different Types of Strong Acids in Various Concentrations

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ABSTRACT

This work proposes a pre-treatment to Nafion® 117 membrane with different acids in various concentrations. The main goal of this study is to increase the membrane hydration, which is determined by the amount of water molecules it incorporates. It is well known that the membrane hydration directly affects its conductivity. Based on many studies that were published regarding this issue, we developed a treatment testing the acids proposed in the research works in order to find a difference between the acids and the effect of the concentrations. In addition, Perchloric acid was also studied. Our work was developed using five strong acids treatments -Nitric, Sulphuric, Perchloric, Phosphoric and Hydrochloric acid- in six different concentrations: -0.025 M, 0.05 M, 0.25 M, 0.5 M, 0.75 M and 1 M. Analyzing the results after an exhaustive study, the membrane shows a similar behaviour when it is treated with different strong acids, incorporating between 16 to 21 molecules of water depending on the concentration of the acid that was chosen. The effect of the different concentrations is remarkable, which leads to the conclusion that the best treatment is to use solutions 0.025 M and 0.05 M (twenty times more diluted than the most concentrated solution tested in the experience). Another effect to be taken into account when the Membrane Electrode Assembly (MEA) is joined in a following step, is the fact that after membrane hydration its size increases by 10 percent (average).

1. Introduction

Nafion membrane was developed in the 1960s and, nowadays, it is the most well known material of this type, consisting of perfluorinated polymer backbone and branches that end in sulfonic acid groups. Nafion acid groups and sorbed water are surrounded by a hydrophobic matrix of tetrafluoroethylene backbone and perfluorovinyl ether pendant side chains. Water sorption swells the hydrophilic domains providing paths for proton transport and water diffusion through hydrophobic domains [1].

Nafion membranes are widely used for Proton Exchange Membrane (PEM) fuel cells and water electrolyzers. The membrane performs two functions, as separator and as solid electrolyte in a variety of electrochemical cells with the main purpose of transporting cations across the cell junction, selectively. Over the last years the interest in Nafion has grown due to the good performance that it shows as a proton conducting membrane in fuel cells. This result takes the lead and is the first in studying proton conductivity, water management, hydratation stability at high temperatures and thermal stability [2].

Nafion membranes have been extensively characterized with respect to their structure, properties and mechanism of proton conduction. The proton conductivity of this material is strongly dependent on the presence of water and it can reach above 0,1 S cm-1 under fully hydrous conditions [3]. Therefore, it is appropriate to consider the existing relation between the membrane conductivity and the water content in the structure.

A recent study of water content considered the thermodynamic forces that affect the sorption of water in the Nafion membrane. The results showed the existence of a critical pore radius below which water is unstable and a critical length below which a pore cannot be filled. Another relevant result in this study is that in a saturated liquid enviroment much smaller pores are filled with liquid. This result is useful to understand the conditions in which Nafion absorbs much more water, which is in contact with saturated liquid as opposed to saturated vapor [4].

Many research works have explained different treatments to increase the content of water molecules in the structure of the membrane. Based on those publications and previous studies [5], a specific acid treatment was performed in order to activate the membrane and increase the amount of water molecules per sulfonic group.

For a better comprehension of this issue, it is important to study the morphology of the Nafion's structure. Naming four of those who proposed the structure of this membrane, there are Eisenberg [6], Gierke [7], Mauritz [8] and Yeager [9] models.

According to Gierke model, the membrane is a cluster type containing the aqueous ions imbedded in a continuous fluorocarbon phase. The clusters are interconnected by narrow channels which determine the transport properties of the ions and water. In the meantime, Hsu and Gierke had derived a

semiphenomenological expression for the evaluation of the diameters of the ionic clusters which vary with water content, equivalent weight and type of cation. Their theory also predicts that the short channels connecting two neighboring clusters are thermodynamically stable. On the other hand, Yeager's et al., studied and compared diffusion and water sorption of carboxylated and sulfonated perfluorinated membranes. Cation and water diffusion coefficients are very large in both materials. However, in the carboxylate membrane the diffusion coefficients are even larger and the water sorption is smaller compared to the Nation membrane. This is due to the different clustered morphology of these ion exchange membranes. These authors supposed that the intrusions of fluorocarbon is less frequent in the carboxylate membrane, and therefore, the phase separation is more complete compared to Nafion [10].

Perfluorosulfonic polymers are composed with an extremely high hydrophobicity of the perfluorinated backbone and an extremely high hydrophilicity of the sulfonic acid functional groups. In the presence of water, the sulfonic acid functional groups aggregate to form a hydrophilic domain. When this is hydrated, protonic charge layers by dissociation of the acidic functional groups, and proton conductance assisted by water dynamics occur. While the well connected hydrophilic domain is responsible for the transport of protons and water, the hydrophobic domain provides the polymer with the morphological stability and prevents the polymer from dissolving in water [11].

Even though many experiences considered various forces for convection including external pressure gradient, capillary pressure, osmotic pressures and elastic forces associaed with membrane deformation, a recent study was performed to confirm that the hydraulic permeability increases with the temperature due to both decreased water viscosity and increased hydrophilic volumen fraction. The relation between these parameters is established according to the ecuation 1.

$$Q_w = \frac{k_w}{\mu\, t_m} \Delta P \qquad (1)$$

Where Q_w meaning the water flux, k_w is the membrane permeability, μ is the water viscosity, t_m is the membrane thickness and ΔP is the hydraulic pressure difference.

The results of the study cited in the reference [1] showed that the membrane tested with the 1100 equivalent weight had a permeability circa 4 x 10^{-16} cm^2 at 23 °C and the membrane with equivalent weight of 1000 had a permeability about 40% greater than the previous one. Also, another determination led to the result that the water volume fraction changes by almost 10% while the hydraulic permeability increased by 50-80%. According to the authors, this difference suggests there may be structural changes to the hydrophilic domains with increased water sorption beyond simple volume expansion. The convection of water through Nafion can also serve as a probe to its structure. The hydrophilic domanis form a network through which water flows. The water flux depends on the size and density of the hydrophilic channels.

Another published observation is the mass loss when it is dried at room temperature in contact with the ambient air due to the water absorbed per sulfonic acid group which seems to be independent of the membrane thickness [13].

Enviromental conditions are relevant to make a right analysis. At ambient preasure the membrane dehydrates at temperatures above 100 ºC, resulting in a proton conductivity decay. The acid treatments were performed at 90 ºC and ambient preasure at each step.

It has been demostrated that the water content tends to be the same if the membrane is hydrated and it is also proved that the membrane can regain the water molecules in case it was intentionally dried as the example of the pretreatment when the Membrane Electrode Assembly (MEA) is joined.

Knowing the characteristics that the structure and the morphology provide, an exhaustive study was developed treating the proton exchange membrane with several acids in different concentrations evaluating the performance of each acid incorporating water molecules.

2. Experimental

The experience was developed using Nafion® 117, which means that the nominal thickness is 183 microns and the equivalent weight (EW) is 1100 considering that EW is the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form.

The as-received Nafion® 117 (Du Pont) was cut into rectangular pieces and treated as follows. Firstly, they were weighted and measured considering this as the initial state without any treatment (zero step). Later, the first step was boiled in H_2O_2 3% for 1 hour [12]. Then the membranes were treated with acid for 3 hours. Five acids were tested in six different concentrations. It was brought under Nitric, Sulfuric, Phosphoric, Perchloric and Hydrochloric acid, 0.025 M, 0.05 M, 0.25 M, 0.50 M, 0.75 M and 1 M. Finally, the membranes were treated in destilled water for 3 hours. After each step, the membranes were cooled in destilled water at room temperature for 15 minutes before being weighted and measured.

According to quality statements, the study was performed by duplicate so 12 pieces of membrane were treated with each acid.

One last measurement is made at the end of the experience in order to check that the membrane hydration is mantained in destilled water, we weighted and measured the following day of finishing the treatment.

3. Results and discussion

Membrane treatment with H_2O_2 3% for 1 hour at 90 ºC is highly recommended to eliminate all the organic impurities as it is received. The result is evident when the membrane becomes colorless.

Besides this benefit, an analogous experience was performed treating the membrane with water at 90 ºC for 1 hour in order to compare the influence of H_2O_2 3% in the same conditions. This was the only difference in the procedure mantining the following steps equal for both acid treatments. We found that the initial treatment with H_2O_2 3% instead of water is remarkable in order to gain more molecules of waters during the entire proccess. The results are shown in Figure 1.

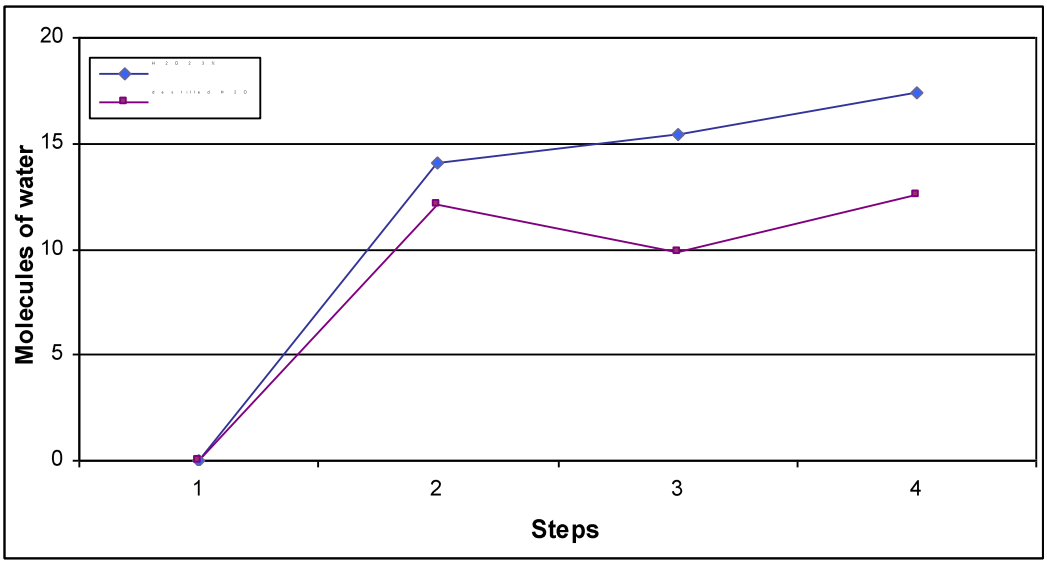

Figure 1. Importance of H_2O_2 3% in the membrane treatment. Treatment steps: 1. Membrane as-received, 2. H_20_2 3% (blue line) and destilled H_20 (purple line) + destilled H_2O 15 min, 3. HNO_3 0,25M (90 ºC for 3 hours) + destilled H_2O 15 min., 4. destilled H_2O (90 ºC for 3 hours) + destilled H_2O 15 min.

Continuing with the investigation, the membranes previously treated with H_2O_2 3% at 90ºC for 1 hour were studied according to the description given before. The results of the acids treatments are shown in the graphics below.

The following tables contain the quantity of water molecules obtained with different concentrations of the proposed acids considering the average (λ_a) value of two samples per acid concentration and the standard deviation (σ) of each measure in porcentual value.

Each table details the quantity of water molecules per sulfonic acid group obtained in the relevant steps of the procedure. These main steps are:

1. Zero
2. H_20_2 3% + destilled H_2O
3. Studied acid in different concentrations + destilled H_2O

4. Boiled H_2O + destilled H_2O

Note: Zero was ommited from the graphics to emphasize the results obtained in the following steps.

Nitric Acid

Table 1. Results obtained in the Nitric Acid treatment with different concentrations.

	HNO_3 0.025 M		HNO_3 0.05 M		HNO_3 0.25 M		HNO_3 0.5 M		HNO_3 0.75 M		HNO_3 1 M	
Steps	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	Σ	λ_a	σ	λ_a	σ
1	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00
2	17,108	0,86	14,708	0,15	14,048	1,74	15,300	0,47	15,683	0,35	15,653	0,40
3	18,613	0,57	18,220	0,57	17,238	0,93	15,489	0,45	16,401	0,46	15,984	0,11
4	16,972	0,21	18,566	0,24	18,080	2,06	17,748	0,01	19,806	0,39	19,131	0,11

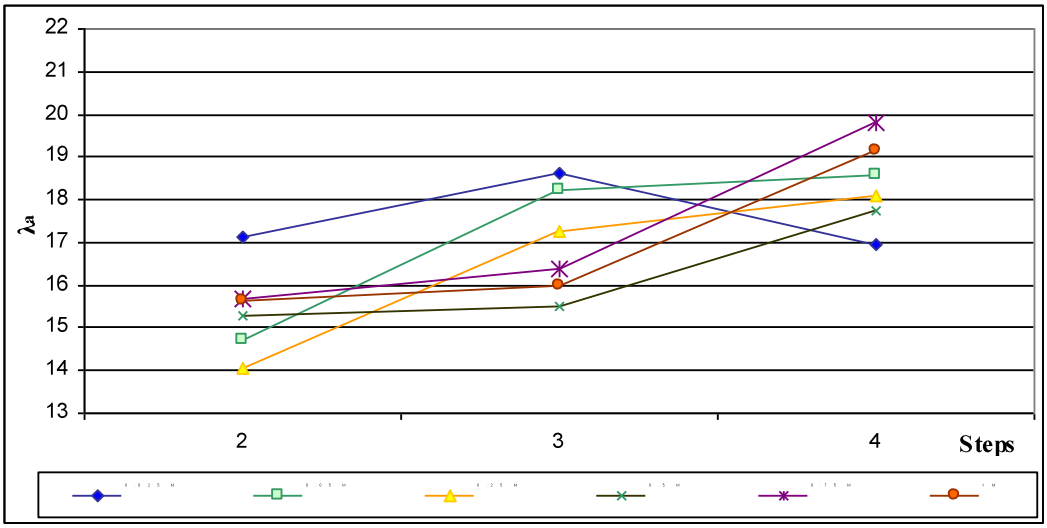

Figure 2. Treatment with HNO_3.

Between the six Nitric Acid concentrations tested during the first study, no significant difference was observed, even though a subtle increment of the water molecules can be noticed in the treatments with lower concentrations.

Sulfuric Acid

Table 2. Results obtained in the Sulfuric Acid treatment with different concentrations.

	H_2SO_4 0.025 M		H_2SO_4 0.05 M		H_2SO_4 0.25 M		H_2SO_4 0.5 M		H_2SO_4 0.75 M		H_2SO_4 1 M	
Steps	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ
1	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00
2	16,768	0,80	15,960	0,89	16,716	0,23	15,157	0,36	16,635	0,23	15,426	0,57
3	18,666	0,75	19,084	0,41	16,933	1,53	15,045	0,51	16,189	0,16	15,251	0,28
4	19,437	0,34	19,784	1,19	18,376	0,29	18,127	0,78	20,499	0,09	18,516	0,04

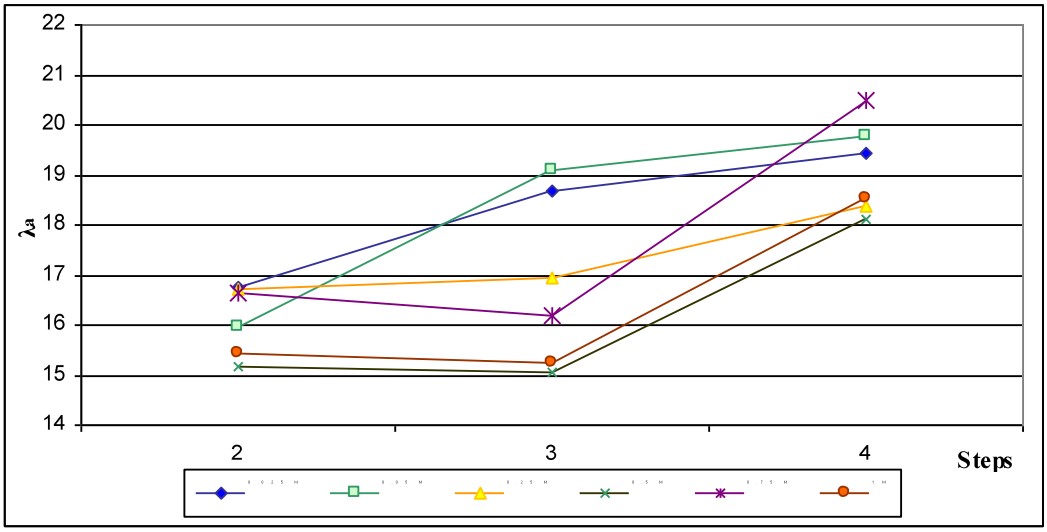

Figure 3. Treatment with H_2SO_4.

The results are similar to Nitric Acid treatment but what is remarkable is the fact that the membrane does not lose any molecules of water in step 3 when it is treated with Sulfuric Acid 0.025 M and 0.05 M.

Phosphoric Acid

Table 3. Results obtained in the Phosphoric Acid treatment with different concentrations.

	H_3PO_4 0.025 M		H_3PO_4 0.05 M		H_3PO_4 0.25 M		H_3PO_4 0.5 M		H_3PO_4 0.75 M		H_3PO_4 1 M	
Steps	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ
1	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00
2	15,870	0,34	17,121	0,48	18,231	0,80	15,876	0,37	16,781	0,66	17,001	0,37
3	17,415	0,49	19,469	0,63	20,564	0,11	18,635	0,46	19,508	0,39	19,951	0,04
4	19,248	0,18	19,966	0,72	21,170	0,06	20,739	0,17	20,198	0,09	21,006	0,14

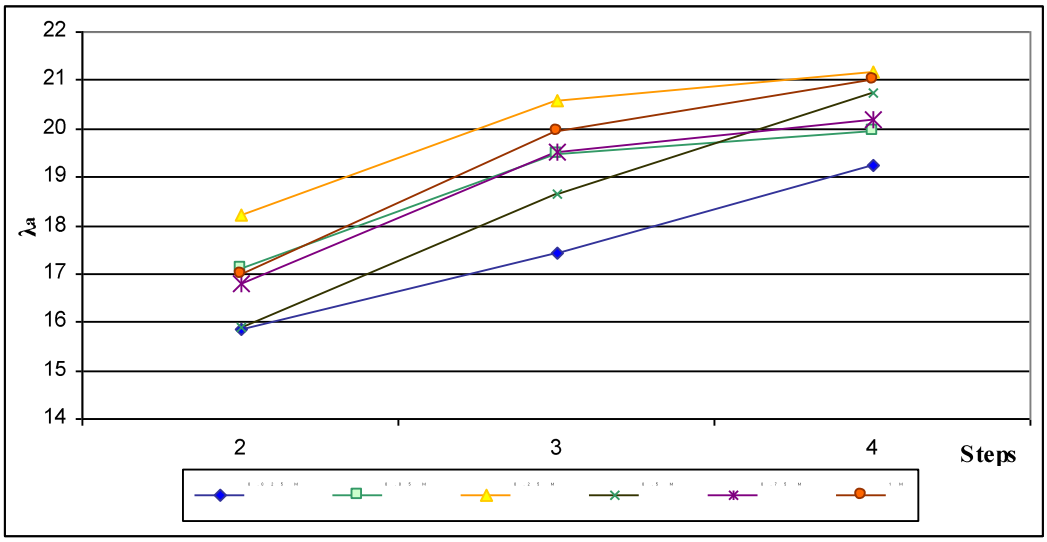

Figure 4. Treatment with H_3PO_4

Even though no result is remarkable comparing with the other acids treated up to now, a subtle improvement can be seen when the membrane is treated with Phosphoric Acid, λ_a is around 21 water molecules per sulfonic acid group.

Another observation to take into account is the fact that the membrane maintains the same tendency when treated with the six different concentrations and it does not lose any water molecules in step 3.

Perchloric Acid

Table 4. Results obtained in the Perchloric Acid treatment with different concentrations.

	$HClO_4$ 0.025 M		$HClO_4$ 0.05 M		$HClO_4$ 0.25 M		$HClO_4$ 0.5 M		$HClO_4$ 0.75 M		$HClO_4$ 1 M	
Steps	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ
1	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00
2	17,068	0,63	18,187	0,11	17,505	0,19	18,694	0,11	16,842	0,25	17,822	0,24
3	18,603	0,70	18,670	0,12	17,536	0,64	17,311	0,02	15,983	0,31	16,000	0,06
4	19,745	0,91	20,116	0,09	20,363	0,14	18,791	1,30	21,197	0,31	20,769	0,25

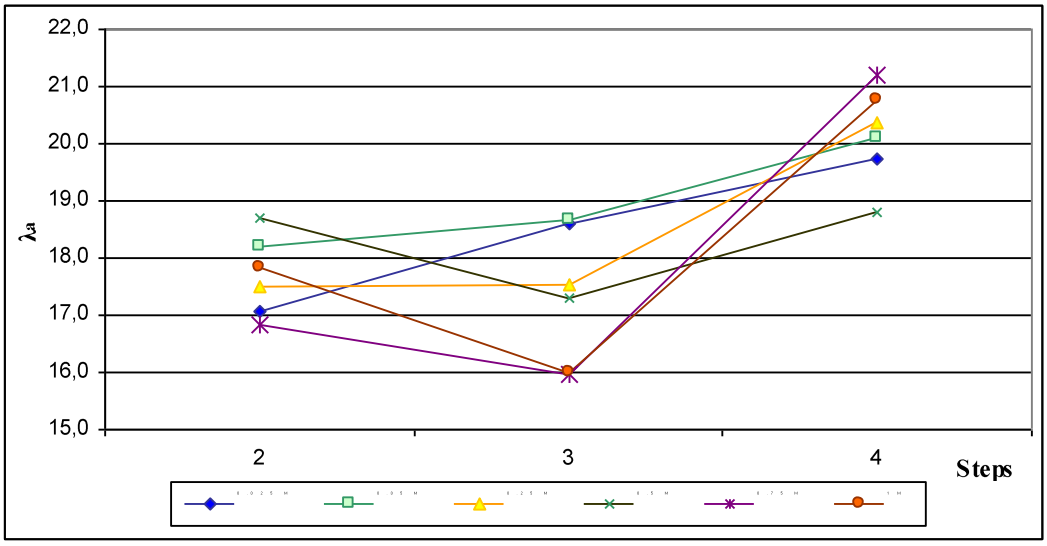

Figure 5. Treatment with $HClO_4$

Figure 5 shows the same tendecy observed with the Sulfuric Acid treatment where the membrane does not lose any water molecules when treated with Perchloric Acid 0.025 M and 0.05M.

Hydrochloric Acid

Table 5. Results obtained in the Hydrochloric Acid treatment with different concentrations.

	HCl 0.025 M		HCl 0.05 M		HCl 0.25 M		HCl 0.5 M		HCl 0.75 M		HCl 1 M	
Steps	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ	λ_a	σ
1	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00	0,000	0,00
2	16,842	0,01	16,186	0,59	16,088	0,13	18,556	0,48	18,523	0,24	17,692	0,15
3	19,409	0,13	19,972	0,81	17,562	0,69	17,849	0,17	17,403	0,04	17,056	0,02
4	21,168	0,07	19,949	0,48	19,911	0,33	20,756	0,31	21,185	0,04	21,890	0,13

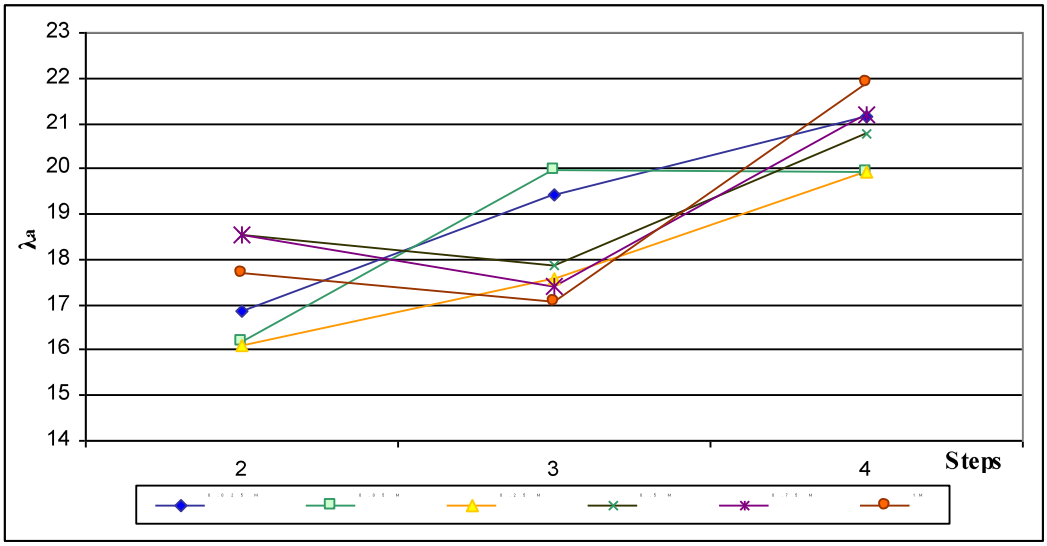

Figure 6. Treatment with HCl

The performance with Hydrochloric Acid is similar to the other acids so no difference between the strong acids tested in this study can be observed. Even though the results of the six different concentrations are similar, what is remarkable is the hydration stability when the membrane is treated with diluted solutions that does not lose water molecules due to the acid treatment at 90 ºC for 3 hours.

Size Analisys

The membrane hydration is visually noticeable because of the increment of its size in a vertical and horizontal way.

During the study, the increment of the size was measured and the results reflect that after membrane hydration its size increases by 10 percent (average). This effect must be taken into account when the Membrane Electrode Assemby (MEA) is joined.

4. Conclusions

The sulfonic acid group has an affinity for water and in contact with it, the sulfonic group dissociates facilitating the proton conductivity. On the other hand, the hydrophobic backbone opposes the increasing water content so an equilibrium state of water content is reached.

The membrane shows a similar behaviour when it is treated with different strong acids, incorporating between 16 to 21 molecules of water when it reaches equilibrium, depending on the concentration of the acid that was chosen and the stability of the temperature during the analysis. The effect of the different concentrations is remarkable regarding the hydration stability, which leads to the conclusion that the best treatments were performed with solutions 0.025 M and 0.05 M (twenty times more diluted than the most concentrated solution tested in the experience). This is shown in figures 7 and 8.

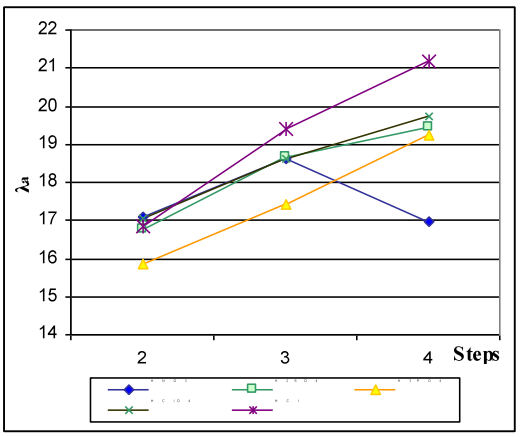

Figure 7. Comparing different acids 0.025 M

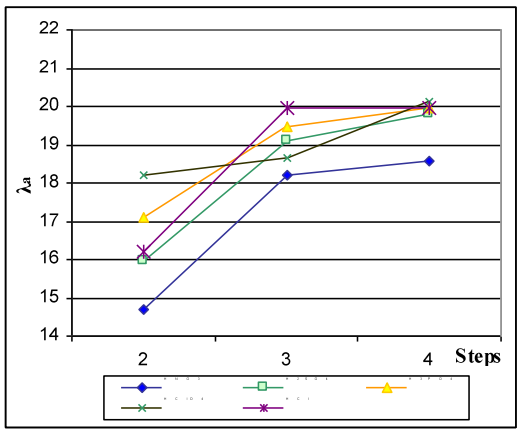

Figure 8. Comparing different acids 0.05 M

The intermolecular forces of the hydrophobic domains are affected in the same way by the different strongs acids studied in this experience. Therefore, it is allowed only to incorporate a certain amount of water molecules per sulfonic acid group and that result has a direct influence on the proton transport and water diffusion.

The effect that the hydraulic permeation increases with increasing temperature was proved.

One effect to be taken into account when the Membrane Electrode Assembly (MEA) is joined in a following step, it is the increasing size by 10 percent (average) when the membrane is hydrated.

An observation that required more study is the hydration stability when the membrane is treated with Perchloric Acid.

5. Akcnowledgements

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6. References

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