

Study of Electrical Resistance on the Surface of Nafion 115[®] Membrane Used as Electrolyte in PEMFC Technology Part I: Statistical Inference

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Received: 11 September 2008 / *Accepted:* 1 December 2008 / *Published:* 20 December 2008

The proton conductive Nafion[®] type membranes with perfluorosulfonic acid as basis are compounds of a polymer belonging to the family of the ionomers. The properties of these materials with respect to those of normal polymers are focused on the interaction ion-polymer in the ionomers allowing among others; conductive characteristics, hence its applications are diverse. The membrane Nafion[®] is commonly used as an electrolyte in the proton exchanging membrane fuel cell (PEMFC). Different kinetic and transport phenomena (mass, electrons and charges) are producing in this electrochemical device during its operation. Particularly, the electrical resistance on the Nafion surface contributes significantly in the phenomena associated with the transport of electrons between the interfaces carbon - catalyst - electrolyte developing a significant effect on the PEMFC performance. This paper presents the statistical analyses results of an experimental design 2³ type with central compound for the records of Superficial Electrical Resistance (SER) measured on both sides of a Nafion 115 (N115) activated and other similar non activated. The statistical results show at 95% confiability, the evidence that process activation produce some modifications in the electrical resistance characteristics on the surface of N115, this includes; decrease in the SER average value in 10 times approximately, the formation of areas with different values SER and a randomization of these regions. Finally, the zones with different levels in ohmic losses may affect the PEMFC performance by non homogeneous conversion of chemical energy in electrical energy and increase of the thermal energy generated in the fuel cell.

Keywords: Nafion, PEMFC, Conductivity, Electrical Resistance

1. INTRODUCTION

In the year 1970, the perfluorosulfonic membranes named Nafion® have been developed by Dupont de Nemours Company. These materials are generated by copolymerization of a perfluorinated vinyl ether co-monomer with tetrafluoroethylene (TFE), resulting in the chemical structure given in Figure 1. Nafion membrane belonging to the family of ionomers i.e. constitutes a cluster ion reaching form a matrix of low dielectric constant causing aggregation of charges in the form of clusters, their existence experimental and theoretical are due to F.C. Wilson in 1968 and Eisenberg in 1970, respectively. Its molecular formula is: $C_7HF_{13}O_5S \cdot C_2F_4$, the molecular weight of this polymer has been difficult to determine with precision, with different values reported over time by different authors, but an estimate has been accepted a molecular weight between 10^5 and 10^6 Da [1-4]. Several molecular models have been published [4, 5]: Yeager, Seko, Pineri, Perusich, Hashimoto, Gierke, Fujimura, Litt Dreyfus, Haubold and Rubatat. However, the generally accepted model is that of Yeager, developed from an analysis of diffusion coefficients for cesium and sodium ions in a Nafion membrane hydrated with a weight equivalent to 1200 [6]. The source of debate on the morphology of Nafion stems from the fact that this ionomer has a unique chemical structure random, being capable of organizing a complex formation of ionic and crystalline regions with significant distribution in size with a wide range of length scales [3, 4]. The Yeager model propose three regions in its structural chain for Nafion membrane (Figure 1): The first of these regions is a structure that contains chains of poly-tetrafluoroetileno (PTFE), inert material in any environment or oxidation reduction with a characteristic hydrophobic and large chemical and mechanical stability [3]. The second region named 'intermediary' is amorphous and hydrophobic, this contains chains hanging, a minimum quantity of water and some radical anions; The third region constitutes briquettes, ionic coexists where most ions sulphonated, cations and water molecules absorbed, giving a absorbing character to the membrane [5]. The sulfate ion present in the structure of Nafion allows the conductive properties in the terms of hydrated membrane state, being an active site where some cations as H^+ , Li^+ , Na^+ among others, spreading by electro-absorption (portering) into the membrane [3]. In particular, water molecule can also spread (mass transit) per share of bipolarity electrical by his hydrogen bridge. Different categories of Nafion membranes have been developed according to their thickness: 118 μm for Nafion 117 (N117), about 100 μm for Nafion 115 (N115) and approximately 50 μm for Nafion 112 (N112) [7].

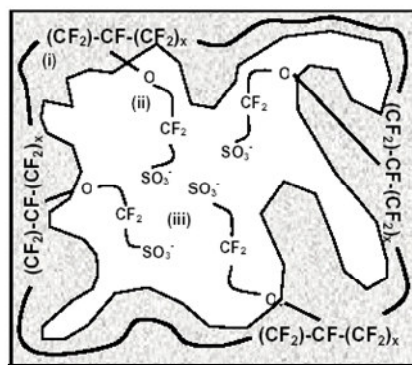


Figure 1. Structural model of Nafion membrane [5].

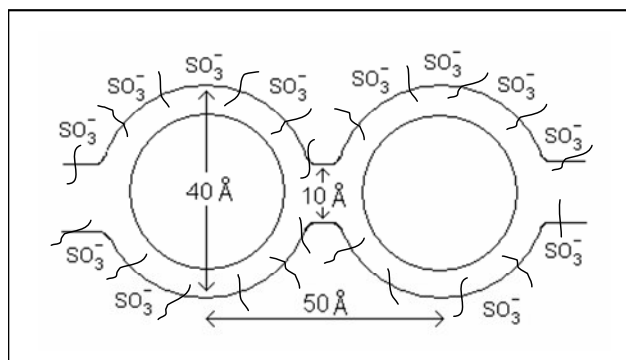


Figure 2. Cluster-Network model for the morphology of hydrated Nafion [3].

During the 70's years of last century, Gierke and collaborators, based on analysis Small Angle X-ray Scattering (SAXS) and Wide-Angle X-ray Diffraction (WAXD) considered the highest prevalence of three models so far determine the morphology of ionomer, including a model of polycrystalline spherical clusters in a lattice, a model of core-shell and a model type lamellar, the authors concluded that the water-swollen morphology of Nafion was best described by a model of ionic clusters that were approximately spherical in shape with an inverted micellar structure. The Gierke's model has allowed predict the number of ions attracted by groups of sulphonated Nafion, as well as the increase in water content [9]. In consideration of the high permeability-ion selectivity and the need for a way to the leaking of ion transport in Nafion membranes, this group later proposed a model of ionic spherical agglomerates; these briquettes are interconnected by narrow channels with certain ionic properties for transport and water, this morphology has a networks briquettes type (Figure 2). The water content in these networks and channels is of great importance to the properties of transport and ionic conductivity of the membrane Nafion [3, 4], given that the vast majority of applications involve a Nafion membranes hydrated or dilated state by a solvent presence.

In a later decades, several research groups [11-15] have reported analysis by ASAXS, SAXS, TEM (Transmission Electron Microscopy) and SANS (Small Angle X-ray Scattering) on Nafion to determine the dimensions of the spatial characteristics of networks briquettes ionic. In general, has been accepted a diameter of 40 Å for briquettes with an average distance from center to center while 50 Å space channels is estimated at 10 Å to conditions completely hydrated, the authors had reported a values minors at this for partially hydrated conditions [3, 4]. Kumar and Pineri reported by mean a study of intermolecular -OH correlations between water and sulphonated groups, a concentration of water in the Nafion equivalent to 21 molecules per $-\text{SO}_3^-$ group [16]. Other studies report increases in the volume of mass Nafion membrane 117 to perform the activation process with values exceeding 30% compared to dehydrated membrane conditions [17]. In a subsequent document Rubatat and co, [18] applied a combination of SAX and neutron scattering techniques, including USAXS to characterize the state in Nafion hydrated within an interval of 1 to 1000 nm. Based on the results obtained, it is considered to be fundamentally characterized by presence of elongated aggregates within the morphology of Nafion. These authors propose that the intermediate values of intervals that

provides information related to the size, shape and spatial distribution of aggregates, while the very small (the small rebound angle) can be attributed to packages largest aggregates with a broad range of heterogeneous distribution. The water absorption allows kernels lengthening forming pools of water surrounded by groups in an ionic polymer-water interface in order to minimize energy interface. As the water content increases the values of the parameters mentioned are increased to approximately 0.3 and 0.5 respectively. At values greater than 0.5 develops a reversal of the structure in such a way that generated the structure resembles a network connected by rods. Lastly, the membrane appears as "dissolve" in solution, the structures are separated bar to get a colloidal dispersion of isolated rods (Figure 3). While this model provided an adequate mechanism for the evolution in the structure with wide acceptance of the concept of isolated groups of the membranes that contain relatively low water content, does not provide justification thermodynamics on the stage of investment. In 2000, Gebel proposed a conceptual description for the process of dissolution for dilation and Nafion membrane [19]. The proposed Gebel is based in SANS results on Nafion in a wide range of water content combined with energy considerations, in this model is considered dry membrane containing ionic isolated groups within an area with a diameter spherical and a distance of downtown center to approximately 1.5 nm to 2.7 nm, respectively.

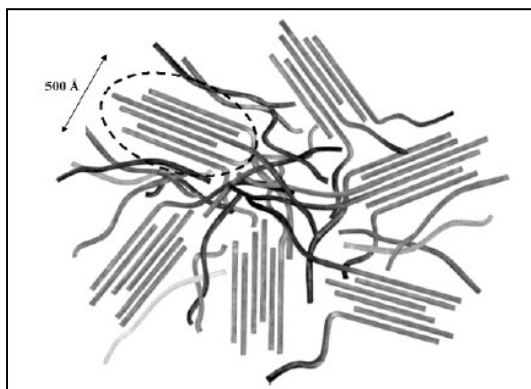


Figure 3. Schematic representation of an entangled network of elongated rodlike aggregates in Nafion [3].

Moreover, interest in the Nafion during recent years stems from the properties involved on the functionality in fuel cells, promising technologies in power generation from chemical energy transformation. Particularly, the proton exchange membrane fuel cell (PEMFC) is considered a clean technology to produce water and electricity at efficiencies above 65%, being considered in stationary and mobile services as the automotive transportation. Specifically, the properties of Nafion membrane involved in the functionality of a PEMFC reported in the literature include: proton conductivity, water management, and stability in the hydration at high temperatures (up to 120°C), electro-osmotic drag, and chemical stability, mechanical and thermal present at the Nafion membrane [5, 7, 20-23]. Moreover, several authors have published the results on ionic conductivity of Nafion® membrane, reporting that overall conductivity in the membrane is a function of the volume in water contained (and hence the relative humidity; % RH) and the sulphation proportion [8-16, 21]. Anantaraman [25] and

Nguy [26] have reported conductivity of $3 \times 10^{-2} \text{ S cm}^{-1}$ to 100% relative humidity. Pourcelli and other authors reported $6 \times 10^{-2} \text{ S cm}^{-1}$ for this property [27, 28], while Tazi and co. reported an ionic conductivity of the membrane N117 equivalent to $1.23 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ in H_2SO_4 1 M a 25°C [29]. Fontanella and co [30] has reported measurements of electrical conductivity from impedance diagrams with values between 0 and 0.10 S cm^{-1} fro N117 and N120 with water content between 3 and 30 wt% respectively.

Hydrogen decomposition takes place in the anodic electrode at the PEMFC into protons and electrons, the protons are driven by the Nafion membrane to the cathode while the electrons are rejected by the polymer electrolyte membrane and driven by an external circuit where their energy can be harnessed in some services. In the cathode, the molecular oxygen decomposes to form water with protons from the membrane and the electrons in the external circuit; the peculiarity is that electrons must overcome the electrical resistance of Nafion to reach at the active sites where the overall reaction is completed. This study proposes a statistical analysis on the electrical resistance measurements at the surface (SER) on the Nafion membranes, in order to know the surface characteristics of this property and the possible effects on the PEMFC functionality. Measurements are made on a membrane N115 without activation and other membrane of the same type and lot previously activated. The statistical tools proposed in this study [31, 32] are; i) descriptive statistics which meet the general characterization to the variable being studied, ii) statistical inference offers insight into the differences between membrane treatments and between its different regions. Finally, a deduction on their effects during the operation of the PEMFC will be discussed.

2. EXPERIMENTAL PART

Two pieces of N115 membrane to the same lot with an area defined in both cases at 112.33 cm^2 ($10.5 \times 10.7 \text{ cm}$), have been used for this study, one of them has been activated in the following manner: a dip in a 3% Vol, H_2O_2 solution at 80°C for an hour, then the membrane is immersed in deionized water to 80°C for one hour, after receiving a bath at the same temperature for two hours in a HNO_3 - 1 N solution, finally apply three bathrooms in deionized water [17]. Both membranes were geometrically divided into 4 quadrants with equivalent area to $5 \times 5 \text{ cm}$ for measurement of SER. An experimental design 2^3 type central compound has been applied for measuring and recording of SER on the membrane N115. Based on the statistical model proposed for this work was designed a matrix with five points (Figure 4) in the Cartesian coordinates (0,0) and the number of entries per quadrant is 13 measurements with a repetition by point to generate statistical report recital 26 entries per quadrant.

The measurement of each point in the matrix was conducted considering units matrix $1 \times 1 \text{ cm}$, using the tips of a multimeter on the edges of each unit as shown in Figure 5. The equipment used for SER measurements was a multimeter BK PRECISION model TEST BENCH[®] 390A. The statistical analysis was carried out in both membranes (activated and not) and on both sides of the same (A and B). The descriptive statistics, inference and statistical analysis were obtained using the software Minitab V.15.

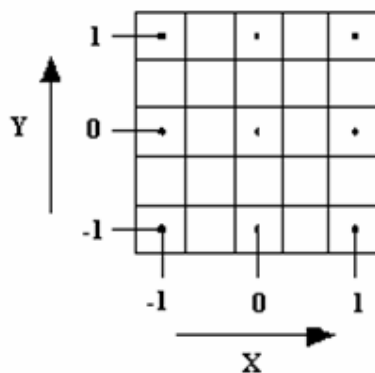


Figure 4. Matrix applied for electrical resistance measurements on Nafion 115 membrane surface.

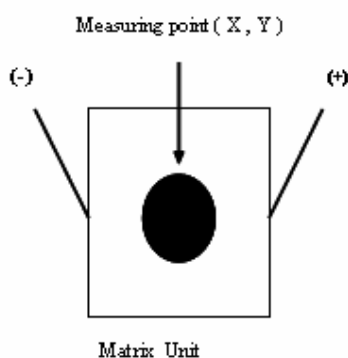


Figure 5. Sketch for matrix unit applied in electrical resistance measurements.

3. RESULTS AND DISCUSSION

Figure 6 shows the membranes N115 used in this study (activated and not). Table 1 shows the increase in volume in the membrane during each stage of activation process. The second piece of N115 has not received any prior preparation. Moreover, a partial reproduction of the measurements of Fontanella and Co. [26] has been adjusted by an exponential function with a correlation coefficient (R^2) of 0.9996 to compare the results in terms of electrical resistance and relative humidity (Figure 7), allowing to locate these conditions in the membranes used.

Table 1. Volume increased after each activation stage process for Nafion 115 membrane.

Nafion 115	Non Activated	H ₂ O ₂ 3% V	H ₂ NO ₃ 1 M	H ₂ O Deionised
Area, (cm ²)	112.33	133.28	133.4	141.36
Volume increased (%)	-----	15.7	16.4	20.5

The values presented in Table 1 shows an increase in the volume set after each activation stage, the first phase being the most far-reaching. The oxidation process caused by H₂O₂ undoubtedly promotes relaxation in the structure of the Nafion membrane, thus the spread of water molecules inside

the membrane causing the increase in volume, 15% for this case in the N115 membrane. However the activation processes for sulphonated sites with HNO_3 not have the same effect on the Nafion 115 structure (only 0.7%V increasing) but it's important for the $-\text{SO}_3^+$ sites activation. Finally, N115 membrane increases significantly in volume (4%) during the third activation stage, using only deionized water at 80°C . The total increase in volume after treatment for activation of the N115 (20.52%) shown in the table above contrasts with the increase reported for the N117 ($> 30\%$) [17], attributed to the absorption capacity depending on the thickness the membrane as we mentioned Kumar and Pineri among others [4, 16].

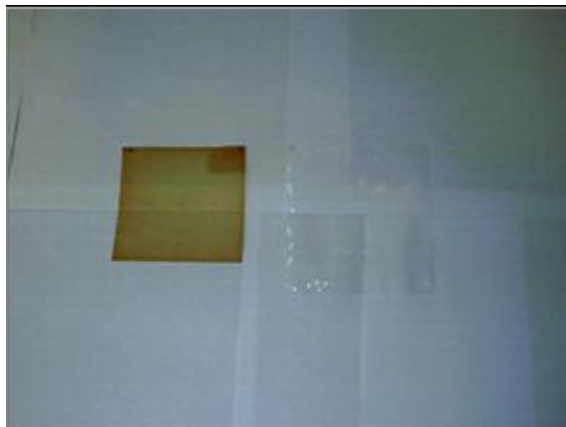


Figure 6. Nafion 115 membranes; activated (translucent) and not activated (dark)

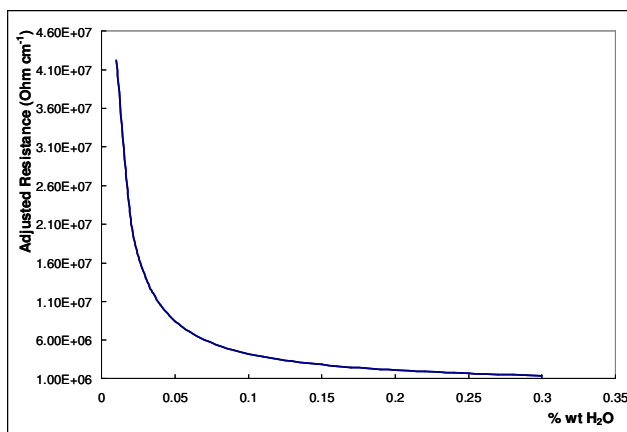


Figure 7. Fontanella's data curve for adjusted electrical resistance in function of water content in Nafion membrane.

3.1. Descriptive Statistics

First, the principles of normality and independence are verified for surface electrical resistance data, confirmation of these principles is important to validate the application of statistical tools in the analysis.

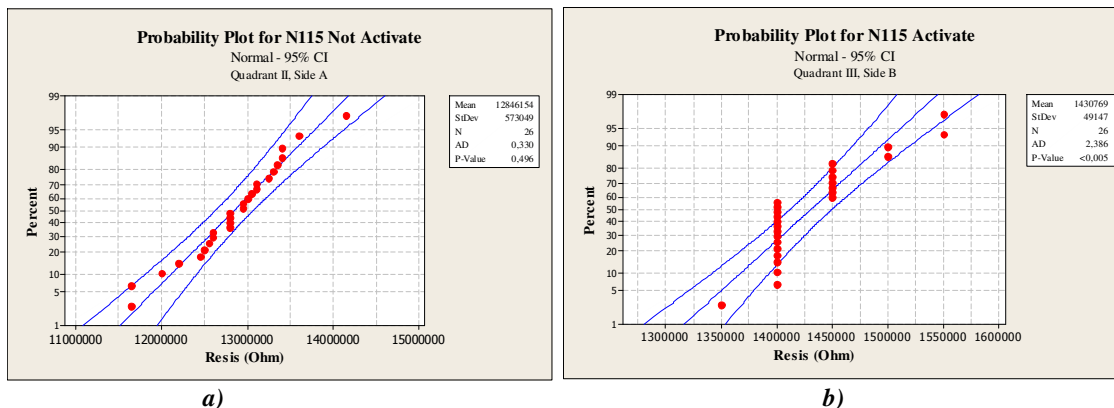


Figure 8. Normality Data Test for (a) the first quadrant side A of not activate membrane and (b) third quadrant side B of activated membrane.

Figure 8.a shows the normality test for the second quadrant side A from N115 dehydrated, not violation for the normally principle is observed on the figure, this behavior being a constant in all cases of the not activated membrane, therefore the reliability of results is robust. In contrast, Figure 8.b shows the normality test for the third quadrant side B in the membrane N115 activated. In this case, there are significant deviations from the normality principle in the SER data; therefore the statistical results should be analyzed with caution. It's important to note the difference between statistical data of both treatments SER membrane N115 (activated and not). Figure 9 shows the independence test for statistical data in the study, the first (a) corresponds to the first quadrant side A of the membrane N115 not activated, no significant deviation is observed in all cases of the dehydrated membrane. Moreover, the picture 9.b shows the same test for the third quadrant side B of activated N115 membrane, slight correlation data is observable on the figure. It should be noted that this behavior occurs in all cases of the membrane activated, indicating a light deviations on the independence principle for SER data for each case. The correlation of data can be attributed to wet conditions and measurement on the surface of the membrane during data record.

Figure 10 shows the histograms of frequency with normality curves for SER data for the first quadrant side A (Figure 10.a) and the fourth quadrant side B (Figure 10.b) for not activate membrane. In both cases, a normal distribution trend is observed, these features were observed in all cases for not activate N115 membrane.

Figure 11 shows the frequency histograms with normality curves for electrical resistance surface data for the first quadrant side A (Figure 11.a) and the third quadrant side B (Figure 11.b) in the membrane N115 activated. Contrary to the characteristics observed for the membrane not activated, in this case is observed an among distant categories (columns) for SER data, i.e., the distribution of data in this case are not continuous, introducing the formation of well-defined groups. It is obvious that the activation process in the membrane N115 alter the structure of the polymer and thus its conductive properties, particularly the electrical resistance surface. These results suggesting the areas formation with different characteristics and properties on the surface for Nafion 115 membrane based on their morphology, in accordance with those reported by Rubatat and colleagues (Figure 3).

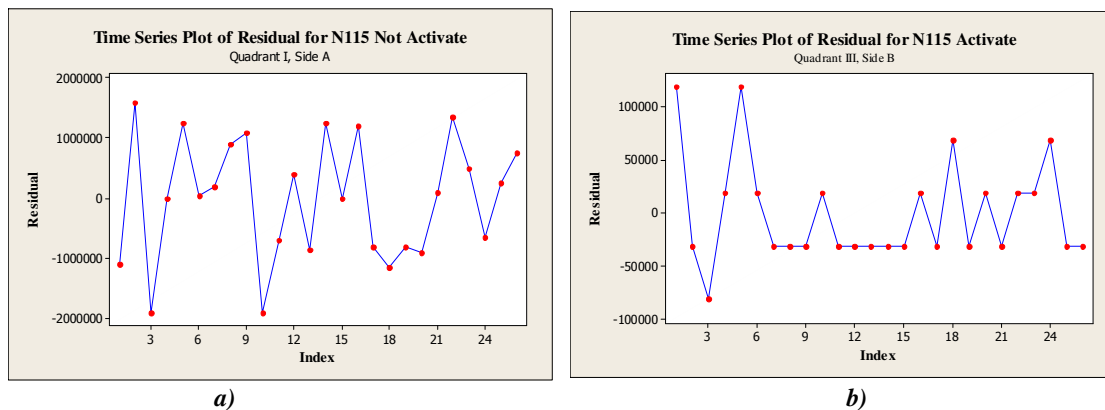


Figure 9. Independence data test for a) the first quadrant side A and b) third-hand quadrant B of the activated membrane.

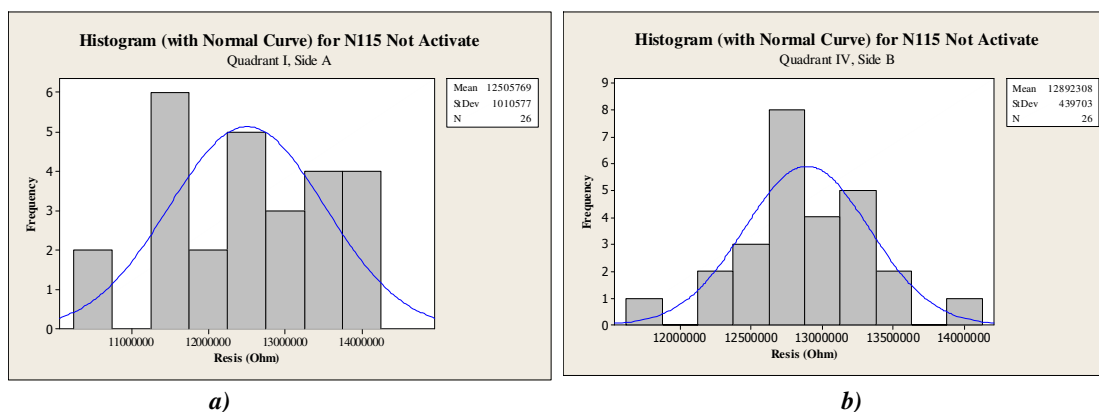


Figure 10. Histogram frequency with normal curve for a) the first quadrant side A and b) third quadrant side B (b) of activated membrane.

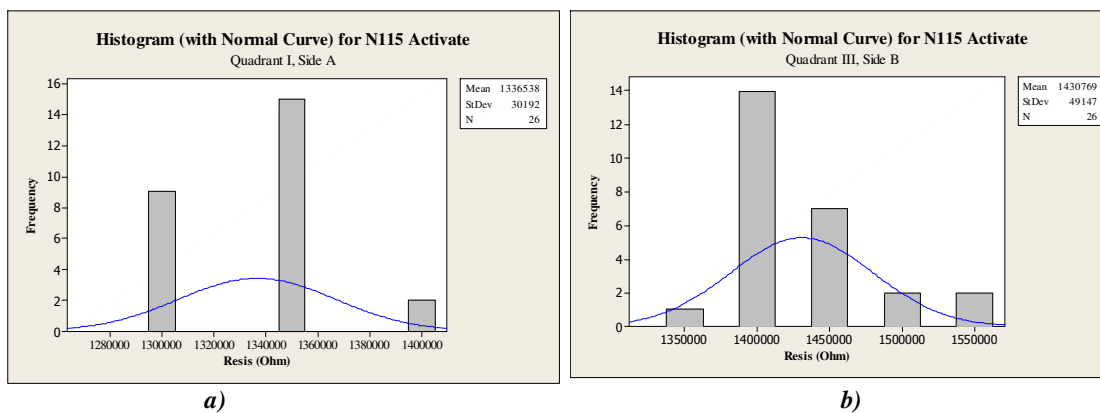


Figure 11. Histogram frequency with normal curve for a) the first quadrant side A and b) third quadrant side B of activated membrane.

Table 2 shows the descriptive statistics obtained with the software MINITAB for not activated Nafion 115 membrane. In general, average values for SER on the surface for N115 not activate are $1.275 \text{ E}^7 \Omega \text{ cm}^{-1}$ for side A and $1.29 \text{ E}^7 \Omega \text{ cm}^{-1}$ for side B, also there are a significant dispersion values presented to the average of standard deviation $7.97 \text{ E}^5 \Omega \text{ cm}^{-1}$ and $5.27 \text{ E}^5 \Omega \text{ cm}^{-1}$ for sides A and B respectively. Moreover, there are values of the median $1.275 \text{ E}^7 \Omega \text{ cm}^{-1}$ and $1.285 \text{ E}^7 \Omega \text{ cm}^{-1}$ respectively which indicate a displacement in the average values to higher values. Comparing the average value of SER with the curve in Figure 7, the not activated Nafion 115 membrane used in this study have around 0.035 wt% of H_2O . This result has no application for PEMFC in working conditions; however the values and averages presented here represent a benchmark for fuel cells and stacks not operated by long time.

Table 2. Descriptive statistics for SER data on N115 membrane for both sides and treatments

NAFION 115 Non Activated Quadrant	SIDE	N	AVERAGE Resistance (Ohm)	STD. DEVIATION (Ohm)	MEDIAN (Ohm)
1 st	A	26	1.25E+7	1.01E+6	1.26E+7
2 nd	A	26	1.28E+7	5.73E+5	1.29E+7
3 th	A	26	1.31E+7	7.09E+5	1.29E+7
4 th	A	26	1.26E+7	8.99E+5	1.26E+7
1 st	B	26	1.30E+7	4.92E+5	1.30E+7
2 nd	B	26	1.29E+7	6.82E+5	1.28E+7
3 th	B	26	1.28E+7	4.85E+5	1.29E+7
4 th	B	26	1.29E+7	4.40E+5	1.28E+7

Table 3 shows the descriptive statistics obtained by the MINITAB software for the activated N115 membrane used in this study. The activated membrane shows a SER average to $1.54 \text{ E}^6 \Omega \text{ cm}^{-1}$ for side A and $4.44 \text{ E}^6 \Omega \text{ cm}^{-1}$ for side B. These values show a reduction in the electrical resistance on activated N115 membrane by 10 times in comparison with not activated membrane. The average values for the standard deviation are $3.03 \text{ E}^5 \Omega \text{ cm}^{-1}$ and $1.18 \text{ E}^5 \Omega \text{ cm}^{-1}$ for A and B sides respectively, noting also a reduction equivalent to 10 times compare with the values present in the dehydrated membrane. Moreover, the values of the median in this case are curtailed in the same order with securities equivalent to $1.48 \text{ E}^6 \Omega \text{ cm}^{-1}$ and $1.37 \text{ E}^6 \Omega \text{ cm}^{-1}$ for A and B sides respectively. In other way, different average values for superficial electrical resistance suggests an effect on the functionality of the PEMFC depending on the side in contact with cathodic or anodic electrode, however the median value does not determine any significant difference but the high values in standard deviation suggest areas with different SER values, in consequence an effect on the PEMFC performance is possible.

The water weight differences at both sides in the not activated membrane are negligible and then both sides are estimated to be worth 0,035 wt% H_2O in Figure 7. In accordance with the literature, the SER is reduced during activation process in the membrane due to the water spread and chemical activation to sites $-\text{SO}_3^+$ inside the Nafion membrane. The difference in the average values for SER at not activated Nafion 115 membrane manifest differences attributable to the morphological conditions in the N115 but these differences may be reduced significantly during the activation process. In

contrast, considering the average values for SER and locating these values in the curve on Figure 7 are worth 0,285 and 0,095% wt% of H₂O for the sides A and B respectively in activated Nafion 115 membrane used in this study. This increase is attributed to chemical activation process in membrane where it favors the water spread inside to the membrane. It is surprising to note a significant difference in water absorption by N115 membrane at each of its sides, which can be attributed to different morphological characteristics in each of its sides depending on the content in PTFE type structures at both sides on the Nafion membrane.

Table 3. Descriptive statistics for SER on N115 membrane for both sides and treatments.

NAFION 115 Activated Quadrant	SIDE	N	AVERAGE Resistance (Ohm)	STD. DEVIATION (Ohm)	MEDIAN (Ohm)
1 st	A	26	1.34E+6	3.02E+4	1.35E+6
2 nd	A	26	1.31E+6	2.26E+4	1.30E+6
3 th	A	26	1.37E+6	2.93E+5	1.30E+6
4 th	A	26	2.15E+6	8.67E+5	1.97E+6
1 st	B	26	1.45E+6	3.28E+5	1.40E+6
2 nd	B	26	1.35E+7	2.64E+4	1.35E+6
3 th	B	26	1.43E+6	4.92E+4	1.40E+6
4 th	B	26	1.39E+6	6.88E+4	1.35E+6

3.2. Statistical Inference: averages analyses.

Table 4 shows the statistical inference results concerning averages on both sides of the membranes N115 (activated and not). The criterion for evaluating inference mean considered is as follows:

Null Hypotheses	Alternative Hypotheses	Reject Null Hypotheses if:
$\mu_1 = \mu_2$	$\mu_1 \neq \mu_2$	P < 0.05

Significance levels at 95% of reliability in Table 4 for the average inference shows the null hypotheses is accepted for second, third and fourth quadrants in not activated N115 membrane (N/A) and only in the first quadrant the null hypotheses has been rejected, i.e.; the average SER values is statistically different only in both sides at the first quadrant, being similar in the others cases on not activated Nafion 115 membrane. In contrast, for activated Nafion 115 membrane (A) used in this study, the null hypotheses is rejected in second and fourth quadrants, however the null hypotheses is accepted in first and third quadrants, i.e.; average values for the SER are statistically different between the both sides in second and fourth quadrants on the activated membrane but the others quadrants presents a similar average values for SER. These results confirm that different affectation levels may

be produced by the activation process on the Nafion surface and each area may be affected in function as dominant type structure on the Nafion surface. En consequence, the difference between SER values at both sides on N115 suggests a probably significant effect on the PEMFC functionality in according to the side in contact with electrodes. Moreover, it's expected a different PEMFC performance by each one quadrant applied in the fuel cell.

Table 4. Statistical inferences about averages for SER on N115 membrane for both sides and treatments (activated and not).

Nafion 115 Quadrant Condition	SIDE COMPARATION	N	AVERAGE Resistance (Ohm)	STD. DEVIATION (Ohm)	P VALUE
IQ-A	A-B	26	1.34E+6 1.45E+6	3.02E+4 3.28E+5	0,092
IIQ- A	A-B	26	1.31E+6 1.35E+6	2.26E+4 2.64E+4	0,000
IIIQ-A	A-B	26	1.37E+6 1.43E+6	2.93E+5 4.91E+4	0,272
IVQ-A	A-B	26	2.01E+6 1.40E+6	8.65E+5 6.88E+4	0,003
IQ- N/A	A-B	26	1.25E+7 1.30E+7	1.01E+6 4.92E+5	0,045
IIQ- N/A	A-B	26	1.28E+7 1.29E+7	5.73E+5 6.82E+5	0,852
IIIQ- N/A	A-B	26	1.31E+7 1.28E+7	7.09E+5 4.85E+5	0,133
IVQ- N/A	A-B	26	1.26E+7 1.29E+7	8.99E+5 4.40E+5	0,115

Q = Quadrant ; (N/A) = Not activated membrane ; (A) = Activated membrane

3.3. Statistical Inference: variance analysis

Table 5 presents the statistical inference concerning to variance analysis for both sides and two treatments at the Nafion[®] 115 membrane (activated and not). The criterion for statistical validation in this case is as follows:

Null Hypotheses	Alternative Hypotheses	Reject Null Hypotheses if:
$\sigma_1^2 = \sigma_2^2$	$\sigma_1^2 \neq \sigma_2^2$	$P < 0.05$

The P values in Table 5 indicate at 95% confidence, the acceptance for the null hypotheses only in the comparison for the second and third quadrants at the not activated N115 membrane (N/A) and rejected in other cases, i.e.; the variance at both sides in second and third quadrants on not activated membrane may be considering statistically similar but not in the other cases. The variance inference for the activated Nafion 115 membrane observes that the null hypothesis is only accepted for the second quadrants and has been rejected for the other cases, i.e.; the variance at both sides in the

activated membrane is similar only in the second quadrant. The results in table 5 suggest in first time a most common levels for SER variance values at both sides on the surface of Nafion 115 membrane and in second time is probably the modifications on the SER variance in all regions (quadrants) for the N115 during the activation process as a result of the morphological characteristics in the membrane, the diffusion of water and chemical activation in $-\text{SO}_3^+$ sites inside the membrane.

Table 5. Statistical Inferences about the standard deviation for SER on N115 membrane for both sides and treatments (activated and not).

Nafion 115 Quadrant Condition	SIDE COMPARATION	N	STD. DEVIATION (Ohm)	P VALUE
IQ-A	A-B	26	3.02E+4 3.28E+5	0.000
IIQ- A	A-B	26	2.26E+4 2.64E+4	0.447
IIIQ-A	A-B	26	2.93E+5 4.91E+4	0.000
IVQ-A	A-B	26	8.65E+5 6.88E+4	0.000
IQ- N/A	A-B	26	1.01E+6 4.92E+5	0,001
IIQ- N/A	A-B	26	5.73E+5 6.82E+5	0,390
IIIQ- N/A	A-B	26	7.09E+5 4.85E+5	0,063
IVQ- N/A	A-B	26	8.99E+5 4.40E+5	0,001

Q= Quadrant; (N/A) = Not Activated ; (A) = Activated

Figure 12 presents the variance test for SER data obtained on the N115 membrane not activated for the first quadrant and both sides. The picture at the top represents the magnitude of the variance of data; it's possible to observe a biggest variance in side A with an interval independent to those for side B, while the variance for side B is focusing it toward lower values. At the bottom of the same figure (12.a) there is the box and whiskers graphic of variance distribution data for the first quadrant and both sides. The SER data distribution is largest for side A with a trend for lowest values; in contrast the data variance distribution data for side B is focused to highest values. These results and P value demonstrate the difference between the two sides regarding their SER values. Moreover, the figure 12.b presents the same test for the second quadrant for dehydrated membrane, in this case the graphs show similar variances with overlapping distribution ranges between both sides, while the variance distribution data (box and whiskers) is observed with slightly higher trend towards values for side B, however the value P indicates a statistical similarity between both sides for the second quadrant of not activated membrane For the third quadrant, the variance test is presented in Figure 12.c where it's observed similarity with the second quadrant in overlapping distribution ranges between both sides being equivalent but in this case, the variance in side A is largest and the trend in data distribution (box

and whiskers) in side B is displaced at smallest values. The variance test for 4th quadrant for both sides is shown in Figure 12.d; their observations are very similar with those for 1st quadrant, therefore a real similarity in SER is supposed for both quadrants in their sides respectively.

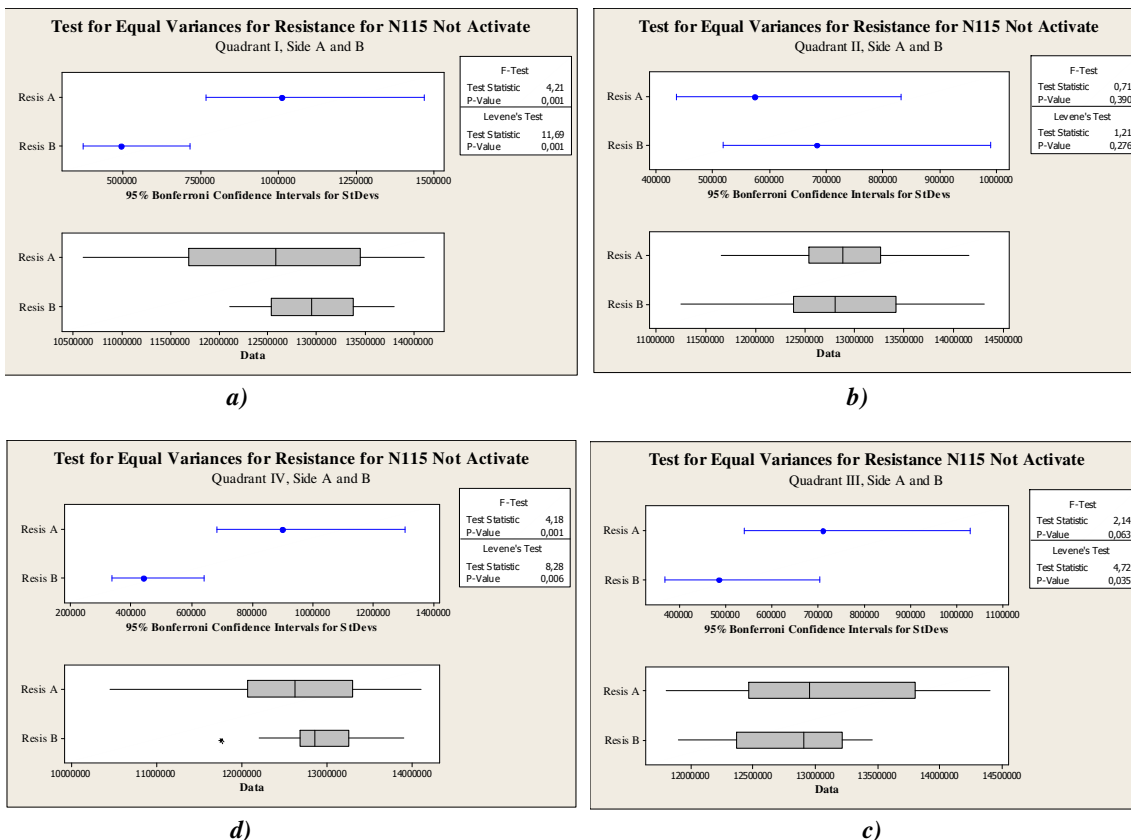


Figure 12. Test for equal variances for SER on N115 not activated in the a) first, b) second, c) Third and fourth quadrants by both sides.

The variance tests for all quadrants studied in the N115 membrane activated are shown in Figure 13. It is possible to observe significant differences between the variances by side in quadrants I, III and IV (Figure 13.a, c and d) in the membrane, where they appreciate different magnitude intervals and total independence (without overlapping). However, there is a significant difference on the first quadrant regarding other cases, the characteristics of the variance are invested on both sides, i.e.; the variance on the side A is smaller and tends to lower values in contrast with others cases. The second quadrant (Figure 13.b) however, shows variances similar in magnitude, with an overlap between the intervals. Moreover, the box and whiskers graphs show inconsistency in the distribution of data variance, therefore any comment has a sufficient level of reliability for some discussion for this case.

In principle, a statistical analysis on the membrane of SER N115 not activate has no practical interest because presents very low ionic conductivity, but the knowledge that provides statistical analysis on this membrane is a very interesting baseline on the results analysis in an activated N115 membrane. Thus the results presented here to demonstrate the presence of different areas of response

to the processes involved in the operation of a PEMFC, i.e.; areas with greater areas of SER generate energy losses for the electrons having contact with the Nafion membrane. These regions submit a higher temperature (hot spots) compared with areas of minor SER. Areas of hot spots could affect the speed of reaction by dehydration membrane and ionic conductivity of the electrolyte, therefore increase ohmic losses and low efficiency of the PEMFC.

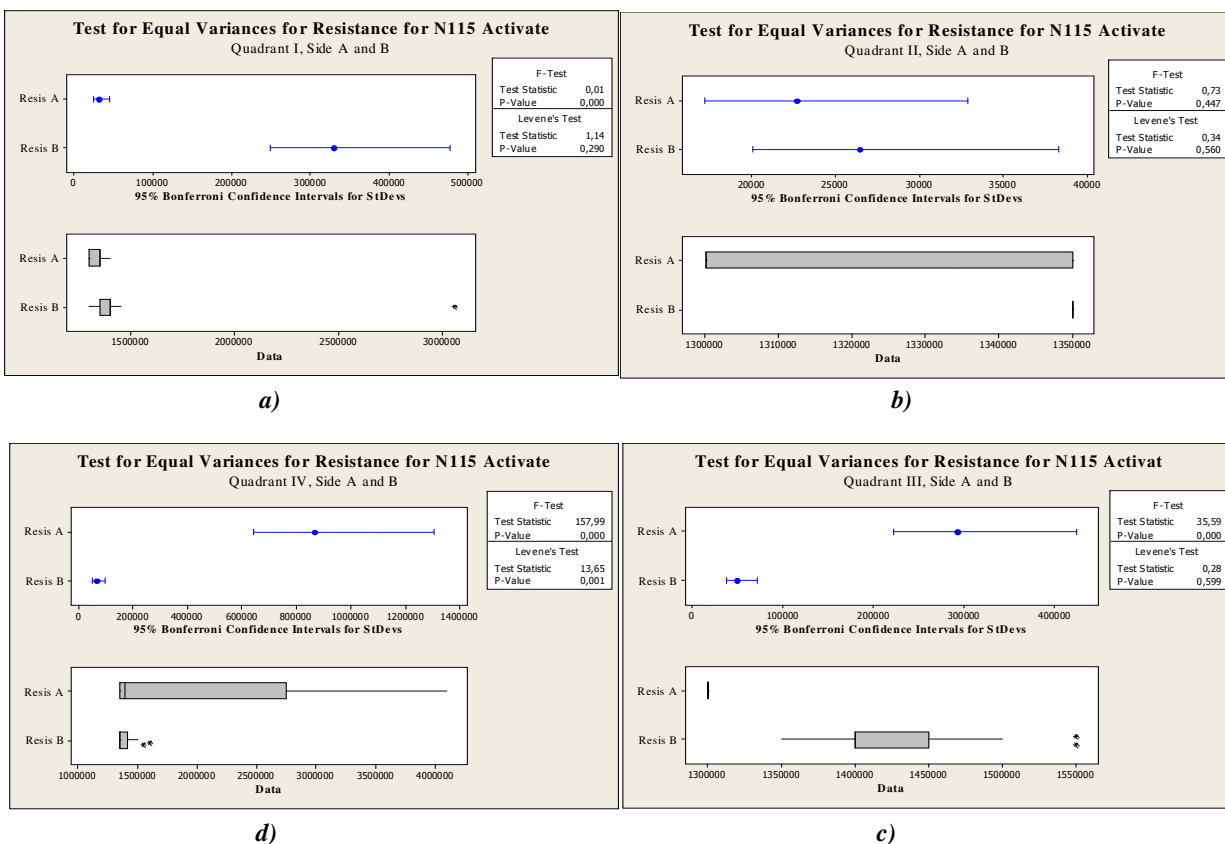


Figure 13. Test for equal variances for SER on N115 activated in the a) first, b) second, c) Third and fourth quadrants by both sides.

4. CONCLUSIONS

The results show the heterogeneity of electrical resistance on the surface of the membrane Nafion 115 membrane for both treatments (activated and not). There is evidence to 95% of superficial changes in the reliability of the variable response after the chemical treatment in the N115 membrane, particularly the SER decreases by 10% during the activation process forming zones with different values and SER distant one another. The activation stages affect the increase in volume and water absorption at different magnitude on the N115 membrane. The statistical inference results show in general, a non homogeneous surface for electrical resistance presenting divers average values for resistance in those areas other than the N115 membrane and even on both sides of the membrane, this behavior being attributable to the structural random diversity in the Nafion membrane as expressed in

the literature. Particularly, the total statistical inference results (average and variance) show a zoning of the area regarding its electrical resistance surface, these areas are also a random structure as proposed by Rubatat and colleagues [18]. The superficial diversity in electrical resistance suggest an important effect on the functionality of the PEMFC directly on increasing ohmic lost in the interfaces electrolyte - catalyst - carbon at the electrode - membrane assembly.

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