MECHANICAL STABILIZATION OF NAFION® MEMBRANE TO FACILITATE THE MANUFACTURE OF THE MEMBRANE-ELECTRODE ASSEMBLIES

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ABSTRACT

During the fabrication of Membrane–Electrode Assemblies (MEAs), the ambient temperature and the humidity have a great influence on the Nafion® membrane generating folds and irregularities on it. As a result, it is normal to obtain a MEA with some folds or wrinkles in the interface of the catalyst layer and on the membrane or on the area of the membrane that was not coated with the catalyst ink. These deformations can cause serious sealing problems in the integration of a fuel cell stack. In this paper a method to mechanically stabilize the Nafion® membrane is presented. This method was applied successfully to Nafion® 117 and 212 membranes and the results from the mentioned treatment are presented.

Key words: MEAs, Nafion membrane, Manufacture, Mechanical stabilization.

1. INTRODUCTION

The Membrane Electrode-Assembly (MEA) is the core of the fuel cell technology, on its catalytic layers the oxidation of the fuel (anode electrode) and the reduction of the oxidant (cathode anode) are carried out to produce electricity. Actually, there are two methods used to apply these catalytic layers: i) deposition of the catalyst layer on the diffuser plate and ii) deposition of the catalyst layer on the membrane [1]. The properties and the performance of the MEA depend directly of the method that was used in its fabrication. On the other hand, the membrane is the more critical component of the MEA, it is very sensitive to the ambient temperature and the humidity. For these reasons the manipulation of the membrane is complicated during the process of fabrication of the MEA. As a result, it is very normal to obtain a MEA with some folds or wrinkles in the interface of the catalyst layer and on the membrane or on the area of the membrane that was not coated with the catalyst ink.

These deformations can cause serious sealing problems in the integration of a fuel cell stack. To eliminate this problem, in this paper a method to stabilize mechanically the Nafion® membrane is proposed. The electrochemical characterization of some MEAs manufactured with membranes treated and without are presented.

2. EXPERIMENTAL

2.1 Fabrication of MEAs

The MEAs were fabricated using the spraying technique. The traditional procedure consists typically in the following steps: a cleaning and chemical activation of the membrane, deposition of the catalytic ink on the membrane using an airbrush and finally a thermo-mechanical process is used in order to increase the binding between the catalyst layer and the membrane. In reference [2] the procedure used in this work for the fabrication on the MEAs is explained with details. In all cases 1mg/cm^2 of Pt/C (20/80 %w) was used as anode and cathode electrode. The active area of the MEAs was 6.25 cm^2.

2.2 Mechanical stabilization method

In general, this method consists of submitting the membrane to a dried process just after the clean and activation process is concluded. During the dried process the membrane is kept warm at 80°C for a period of at least 6 hours in a laboratory stove. After this time the membrane is left to cool at ambient temperature. Then the membrane is submitted to a thermo-mechanical process to a certain time and temperature. The membrane is left again to cool to ambient temperature and can be used to apply the catalytic ink on its surface or to store in a plastic bag to use it later. Reference [3] explains this procedure. With this process, the membrane can remain completely flat during several days independently of the ambient conditions and temperature. This procedure facilitates the manipulation of the membrane during the fabrication process and MEAs without folds or wrinkles.

In order to compare the mechanical stabilization method developed, some MEAs were manufactured using Nafion® membrane 117 and NR-212 treated with and without the mechanical stabilization method. All MEAs were electrochemically characterized. The polarization curves, the electrochemical surface area (ESA) and the micrographics obtained with the scanning electron microscopes (SEM) are presented in the next section.

3. RESULTS AND DISCUTIONS

In Figure 1, MEAs manufactured with and without the use of the mechanical stabilization method are presented. As can be see, the advantage of using the mechanical stabilization method is the MEAs completely flat and free of folds or wrinkles. Also, it is important to mention that this method can be used in the fabrication of MEAs of different sizes whit excellent results.

a **b** **c** **d**

Figure 1. MEAs fabricated using the mechanical stabilization method (**a** and **c**) and without (**b** and **d**). Here is clear to see the convenience to use the mechanical stabilization method to obtain MEAs without folds or wrinkles.

3.1 Polarization curves

Figure 2 shows the polarization curves obtained in the MEAs fabricated with and without the use of the mechanical stabilization method. The experimental conditions were the following; hydrogen and oxygen were used at 10 psi and the temperature of the cell was 70°C. The polarization curves were obtained between -0.1 V (respect to the OCP) up to 0.1 V (respect to the reference electrode) using a scan rate of 10 mV/s.

As can be seen in Figure 2, the use of the mechanical stabilization method in the fabrication of the MEAs does not present notably differences in the performance of the MEAs, only a light decrease in the voltage is observed at current densities of around 1000 mA/cm^2 in the MEA fabricated with the membrane NR-212. On the other hand, it can be seen that the MEAs fabricated with the membrane NR-212 has a better performance than the MEAs fabricated with the membrane 117. This is due to that the membrane NR-212 is thinner and has a better conductivity than the membrane 117. Also the membrane 117 is more susceptible to lost water increasing its resistance. Do to this its performance is lower than the membrane NR-212.

The results here obtained confirm that the use of the mechanical stabilization method in the fabrication of the MEAs not changes drastically the properties and the structure of membrane.

3.2 Electrochemical surface area

The cyclic voltammograms obtained in the MEAs manufactured are show in the Figure 3. To obtain the electrochemical surface area the experiments were carried out at a temperature cell of 35 °C, the anode was fill with hydrogen and the cathode with nitrogen, both gases at 10 psig of absolute pressure. The voltammograms were recorded between 0 and 0.8 V using a scan rate of 40 mV/s.

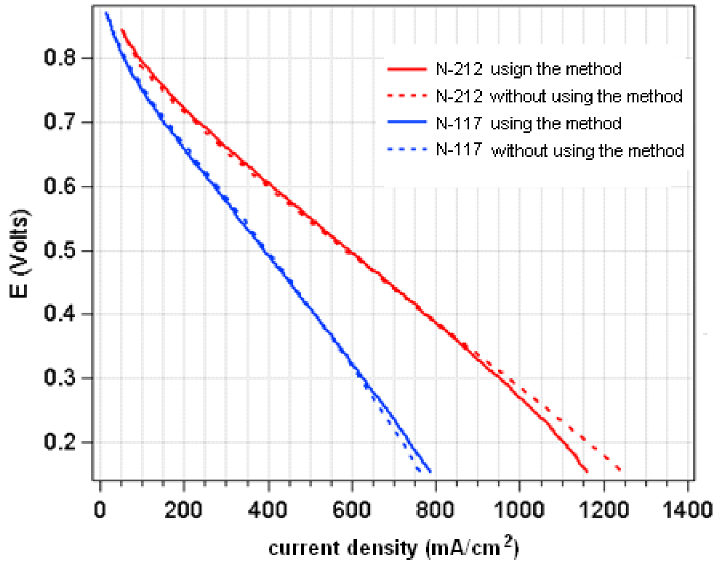

Figure 2. Polarizations curves of the MEAs fabricated with (solid lines) and without (discontinue lines) the use of the mechanical stabilization method. Experimental conditions: hydrogen and oxygen at 10 psi, temperature cell at 70 °C and a scan rate of 10 mV/s.

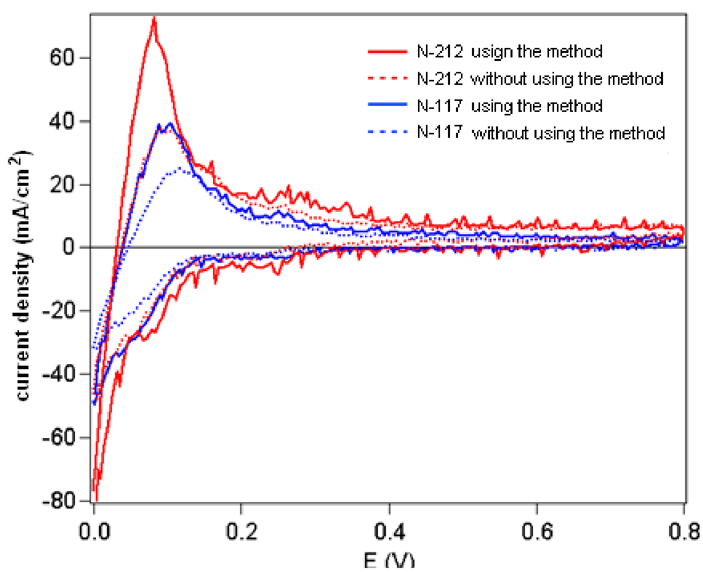

Figure 3. Cyclic voltammograms the MEAs fabricated with (solid lines) and without (discontinue lines) the use of the mechanical stabilization method. Experimental conditions: hydrogen (anode) and nitrogen (cathode) at 10 psi, temperature cell at 35 °C and a scan rate of 40 mV/s.

The electrochemical surface area of the Pt catalyst is calculated from the charge density obtained from the voltammograms (see Figure 3). The procedure of this calculation is described in reference [3]. The obtained values of the ESA are presented in Table 1.

Table 1. Average electrochemical surface area of the MEAs fabricated with and without the use of the mechanical stabilization method.

MEA	ESA (m^2/g Pt)
N-117 without the use of the method	34.27
N-117 using the method	47.71
N-212 without the use of the method	48.71
N-212 using the method	77.81

Apparently the MEAs fabricated with the use of the mechanical stabilization method seem to give a better ESA than the MEAs fabricated without the use of this method, nevertheless it is not possible to see a clear tendency and the dispersion of the values is high. Maybe this dispersion only owes to the differences in the preparation of the MEAs, since what this test evaluates is only the catalytic layer, and due to that all MEAs have the same composition there should not be significant differences in the value of electrochemical surface area.

3.3 Scanning electron microscope

In the Figure 4 is possible to see the different thicknesses of the membranes N-117 and NR-212 of a round of 150 and 40 µm respectively. Also it can be see that the membrane NR-212 is more flexible than the membrane N-117. Observing only the catalytic layers of the MEAs at a magnification of 2000X (see Figure 5), it is possible to see that the MEA N-117 without the use of the method shows a more flat structure than the others MEAs. This structure explains the lowest value of the ESA found in this MEA.

On the other hand, it is possible to see that the MEA N-117 using the method and the MEA N-212 without the use of the method present very similar structures, which agrees with their similar values of ESA found.

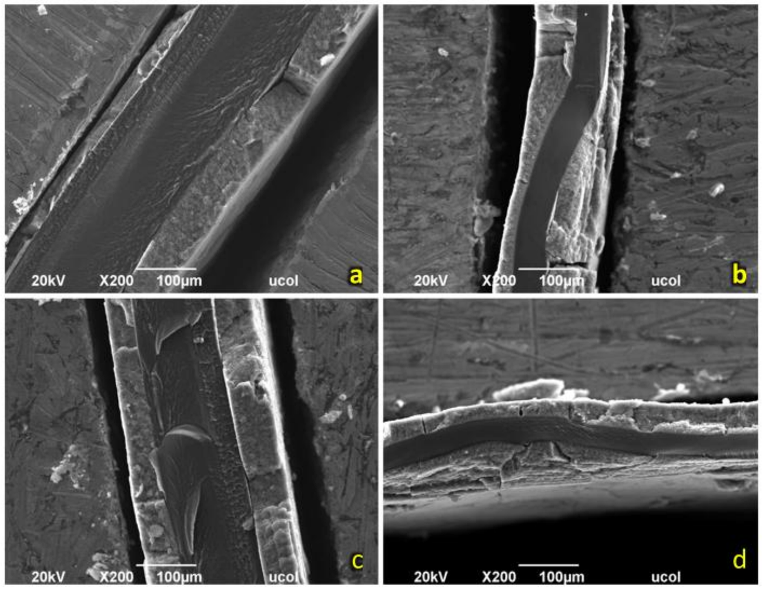

Figure 4. Photography of the cross section of the MEAs fabricated. (a) N-117 using the method, (b) N-212 using the method, (c) N-117 without the use of the method and (d) N-212 without the use of the method. Magnifications 200X.

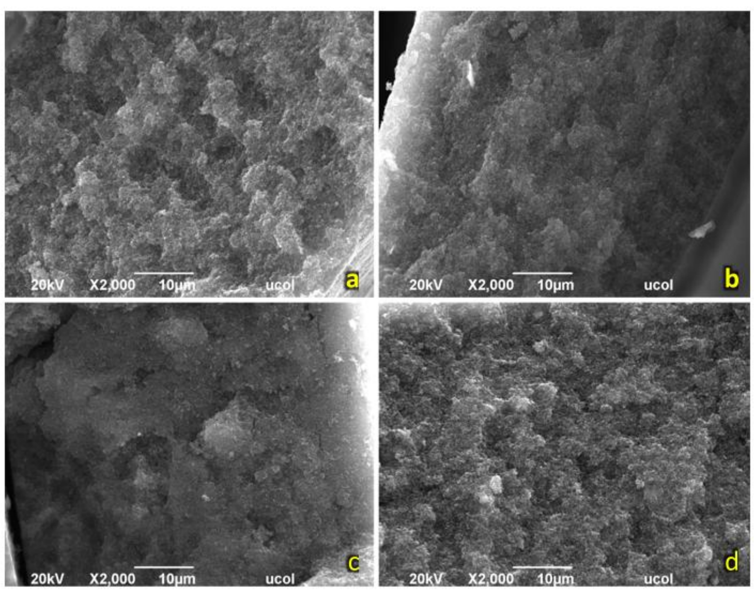

Figure 5. Photography of the cross section of the MEAs fabricated. (a) N-117 using the method, (b) N-212 using the method, (c) N-117 without the use of the method and (d) N-212 without the use of the method. Magnifications 2000X.

The MEA N-212 using the method was the MEA with the highest value of ESA, nevertheless the porous structure that this MEA presents is intermediate to the previous membranes (see Figure 5).

In the Figure 6 a frontal view of the MEAs is presented. Here it is possible to observe that the MEAs N-117 using the method and the N-212 without the use of the method have similar cracks (very open and more or less frequent). On the other hand, the MEA N-117 without the use of the method and the MEA N-212 using the method show a more flat structure with a less quantity of cracks, however, the MEA N-212 using the method shows the cracks more opened than the other MEAs which can explain the highest value of ESA.

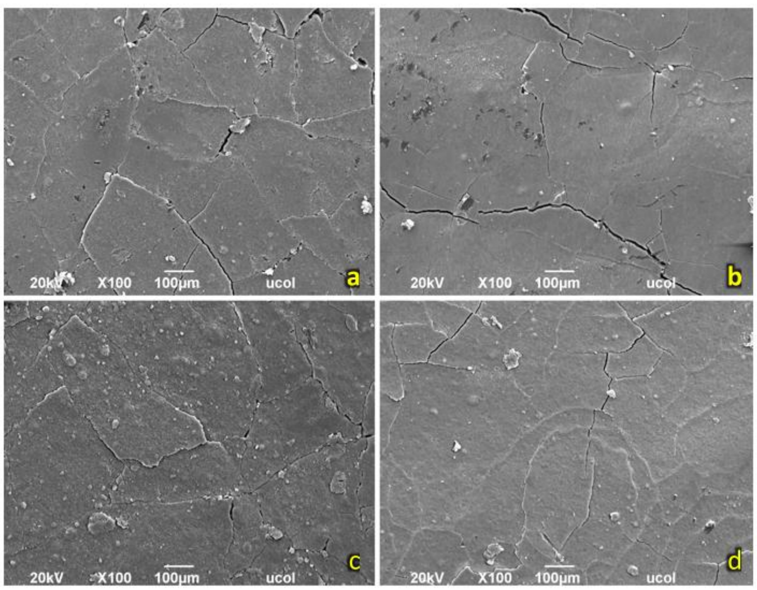

Figure 6. Photography of the frontal view of the MEAs fabricated. (a) N-117 using the method, (b) N-212 using the method, (c) N-117 without the use of the method and (d) N-212 without the use of the method. Magnifications 100X.

4. CONCLUSIONS

The results obtained in this work can be summarized as follow:

- A mechanical stabilization method was developed. Applying this method to the Nafion® membranes, MEAs completely flats and free of folds or wrinkles can be easily obtained, independently of the environmental conditions.

- The use of the developed method facilitates the manipulation of the membrane during the fabrication process of the MEAs and at the same time their integration in the fuel cell stack.
- The mechanical stabilization method does not change the properties and the structure of the Nafion® membranes and very similar performances were found in the MEAs manufactured with membranes treated and untreated.
- The values of the ESA do not show a clear tendency and more experiments are necessary to obtain a final conclusion.
- The obtained micrographies of the MEAs with the SEM were of great help to understand the values of the ESA.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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