Hydrogen-crossover evaluation of graphite bipolar plates and membrane-electrodes assemblies, used in PEMFC. Hardware development and methodology implementation

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ABSTRACT

In this work, we propose a methodology to evaluate hydrogen crossover through graphite bipolar plates (BPP's) and membrane-electrodes assemblies (MEA's). The methodology development includes the design and construction of a dedicated hardware for this test and its application to a batch of 20 BPP's and 20 MEA's newly manufactured. This testing was performed as a measure in the quality control (Q.C.) of materials and manufacturing processes. The methodology is based on the classic electrochemical test for hydrogen crossover evaluation in a H2-N2 system, in which, the hydrogen that manages to permeate the material under test is electrochemically oxidized. The results showed that the methodology was highly effective, achieving quantitatively the evaluation of hydrogen crossover in the tested components with a high precision (standard deviation = 3.53E-5 mL/(min-cm2)) and sensibility. The methodology does not modify the components physicochemical or mechanical properties

Key words: Hydrogen crossover, bipolar plates, membrane-electrodes assemblies

1. INTRODUCTION

PEMFCS failures are in most cases materials related, being the membrane in the membrane-electrodes assembly (MEA) and the graphite in the bipolar plates (BP) the most fragile components and the most susceptible to the thermo mechanical cycles during the system operation. Besides this, the membrane thinness and stress (thermo mechanics) at which it is subjected during the MEAs fabrication process enhances the appearance of ruptures and or pinholes causing hydrogen crossover and short circuit across the membrane. The brittleness of the graphite makes the manufacturing of bipolar plates a delicate process that requires a careful handling during fabrication. The graphite BP, after the flow field is machined, requires gas permeability verification to probe that hydrogen cross over will not occur through the plates.
As part of the quality control in the PEMFC stacks manufacturing at the IIE, a pre-selection of the MEAs and BPs to be stacked together is required to ensure the good state of health of these components.
During fuel cell operation, a drop in the outlet voltage signal is indicative of a failure. Hydrogen crossover can be identified by a decay of the cell´s open circuit as the reaction of crossing hydrogen in the cathode creates a mixed and lower voltage than the expected (c.a.1.0V).

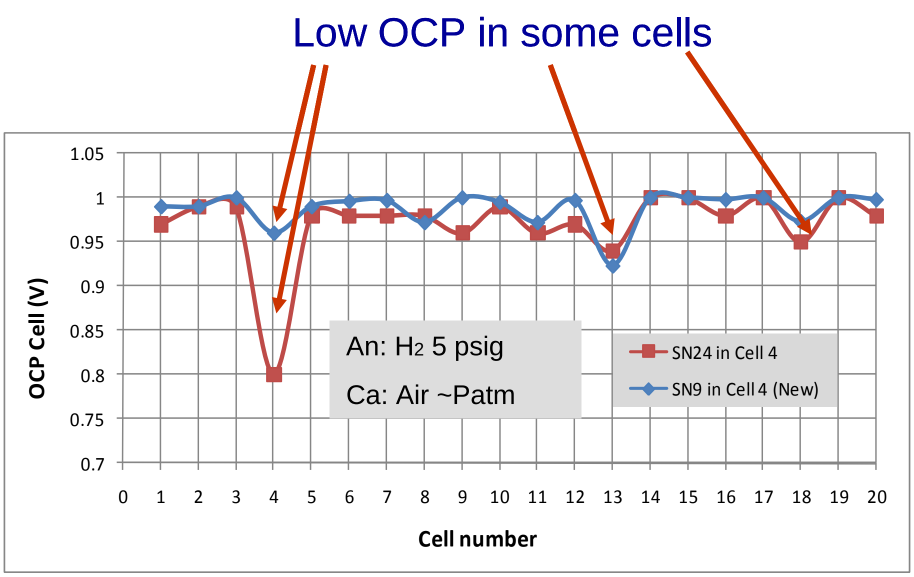

Figure 2. Open circuit Potential measured in a 20 MEAs PEMFC stack

The hydrogen crossover test procedure developed at IIE for MEAs and BPs is based on the identification of hydrogen permeability across the membrane and the graphite plate above the known values for natural permeability in both materials. In this way, when a hydrogen crossover flux is found to be higher than the standard value indicates a crossover caused by a mechanical failure in the sample.

The test is divided by two stages: 1) the identification of gas leaks and crossover by a pneumatic test, and 2) the hydrogen crossover flux quantification by linear sweep voltammetry, a common electrochemistry technique.

The MEAs and BPs crossover tests were carried out, separately, in a hardware built at IIE especially for each test.

2. EXPERIMENTAL

2.1 Hydrogen Crossover in MEAs

The hydrogen crossover hardware for the MEAs is formed by two metallic plates that enclose and MEA with its gass diffusion layer (GDL) electrodes on each side, which created two individual chambers separated by the MEA. See Figure 2. Each chamber is pressurized keeping a pressure gradient not higher than 5 psig. Pressure gauges and ball valves were installed along the inlet gas lines to control the gas supply. The outlet ports had ball valves to allow a controlled gas exhaust.

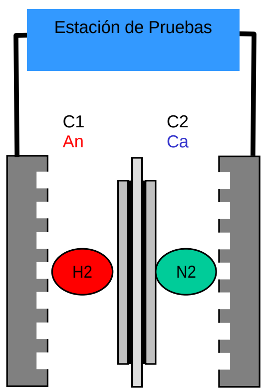

Figure 2. Hydrogen Crossover Hardware for MEAS

For the pneumatic test, to detect leaks and the possibility of crossover, nitrogen was supplied in chamber C1 at 5 psig keeping the outlet ports in both chambers closed. In case of pressure drop, the whole system was first checked for leaks and then for crossover. If C1 shows a relevant pressure drop (above 2 psig) and C2 shows the same increase in pressure, then a crossover flux was confirmed and the MEA could be disregarded. This firs test allows identification of crucial damaged MEAs with such a large hydrogen crossover that the electrochemical test was not necessary.

The second part of the test was applied to quantify the flux of the hydrogen crossover. For this test, chamber C2 was pressurized with nitrogen gas at 2 psig and chamber C1 with hydrogen at 6 psig. The potentiostat was connected to the cell with the following configuration: the working electrode (short circuited with R1) to C2 and the counter electrode (short circuited with R2) to C1.

The cell voltage was swept from 0 to 0.8 V (vs. the counter electrode) with a scan rate of 2 mV/s. During the scan, any hydrogen present in the nitrogen chamber (C2) was oxidized resulting in an increase of the current density at high voltage values. The hydrogen crossover flux was calculated based on Faraday equation that explains the flux linear dependency of the mass transport limiting current:

$$J_{cruce H_2} = \frac{i_{\lim}}{n \cdot F} \qquad \text{(Ec. 1)}$$

where i_{lim} is the limiting current by mass transfer, n the number of electrons in the reaction, and F the Faraday constant (96485 C/electron.mol).

2.2 Hydrogen Crossover in BPs

The measurement of hydrogen crossover in BPs was carried out in a 3-chamber-cell built especially for this test at the IIE. The cell consisted of 3 chambers where the BP to be tested was located in between an MEA and a GDL, all enclosed between two metallic plates. See Figure 3.

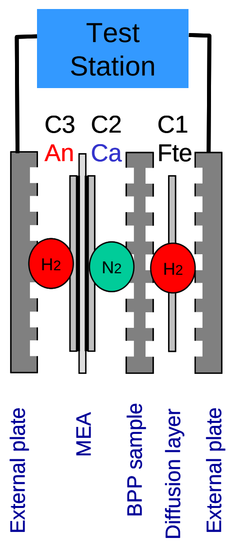

Figure 3. Hydrogen Crossover Hardware for Bipolar Plates

The testing procedure was the same applied to MEAs: a pneumatic test was performed to detect high crossover fluxes and leaks due to sealing; followed, by the electrochemical test for quantification of hydrogen crossover fluxes. For the first test, nitrogen was fed to chamber C2 to detect the possible pressure drop across the BP. For the electrochemical sweeping voltammetry, hydrogen was supplied to chambers C1 (12 psig) and C3 (2 psig); meanwhile nitrogen was fed to C2 (2 psig). The crossover flux was calculated following the Faraday equation in the same way that for the MEAs.

3. RESULTS

In preparation for a 20 cell stack, 20 sets of MEAS with respective BPS were tested for pneumatic and electrochemical tests. A typical curve from the lineal sweep voltammetry for MEAs is shown in Figure 4.

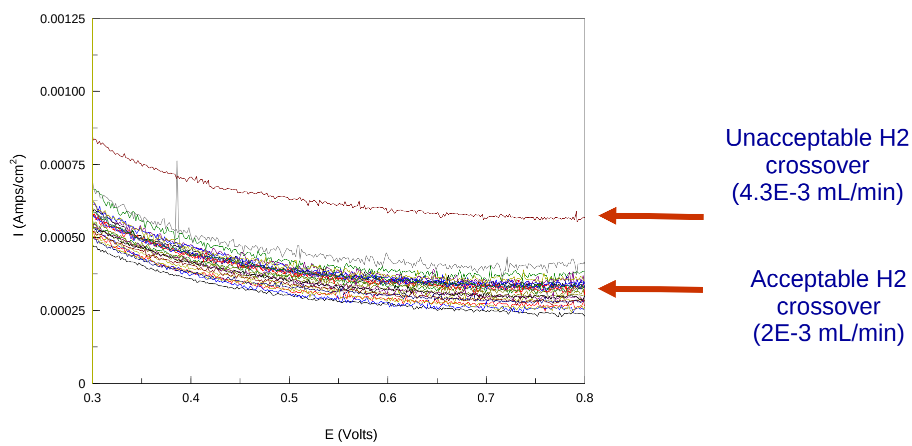

Figure 4. Current density vs. cell potential from Hydrogen Crossover test for 20 MEAs

As observed in Figure 4, the current density shows in all cases a variation with respect to the voltage scan showing an averaged value of $3x10^{-4}$ A cm^{-2} . From the slope of the curves and with the Faraday equation (1), the hydrogen crossover flux calculated averaged a value of 2 x 10^{-3} $mLmin^{-1}$. In the same graph, it is shown an example of an MEA with a higher current density that showed an unacceptable hydrogen crossover flux of 4.3 x 10^{-3} $mLmin^{-1}$; from this result, it could be identified a faulty MEA.

In Figure 5, an example of a short circuit case from a damaged MEA is compared with a group of MEAs in good health state. The increasing slope in the blue line points to an internal resistance tending to infinity. This MEA was then separated from the healthy ones, as the short circuit is indicative of electric contact between the anode and cathode across the membrane due to, either, an immersed conductor or a perforation in the membrane, which makes it a faulty MEA unacceptable for the stack.

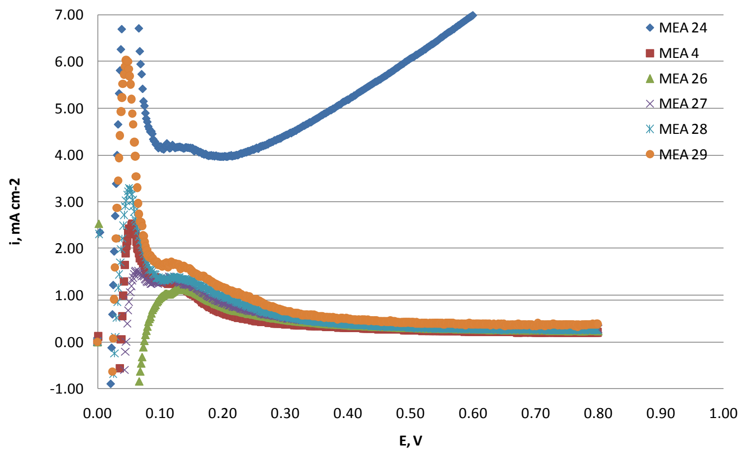

Figure 5. Comparison of a mechanical damaged MEA showing a Short circuit response (blue line) compared with *healthy (*no crossover or short circuit*)* MEAs (coloured).

For the quantification of hydrogen crossover in BPs, a standard MEA was used as reference to compare the voltammetry results from the tested BPs. As seen in Figure 6, the graphs show similar slopes and values for the standard MEA and BPs samples, indicating that the current density was limited by the membrane permeability actually.

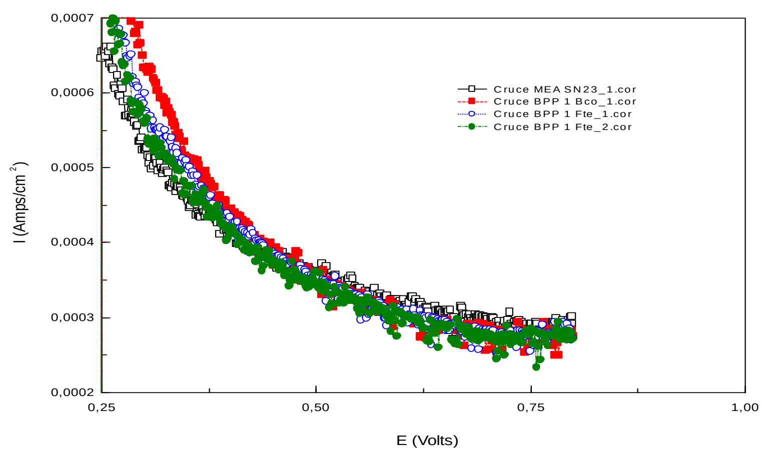

Figure 6. Current density vs. cell potential from Hydrogen Crossover test for BPs

4. CONCLUSIONS

As a result of the need to implement a quality control stage during the manufacturing of low power plants at the Electrical Research Institute a methodology for detecting flowed MEA's and bipolar plates was developed based on the traditional hydrogen crossover test. This methodology allows to identify potential contributions for lower performance of a fuel cell stack which performs optimally in individual MEA testing. Often fuel cell developers integrate components manufactured by third parties. In this case, carbon plates are commercial components that have in-house gas flow field designs machined in our lab, which also might introduce additional factors affecting mechanical properties in both MEA's and bipolar plates components, which makes this type of control testing a necessity

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