

Experimental Decoupling of Single Cell Polarization Losses

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Summary

The decoupling of the current sweep with the Ohmic resistance is a very powerful tool to determine the magnitude of the voltage losses inside of a fuel cell. In a time frame of seconds, the fuel cell can be diagnosed and critical information on the state of the membrane, catalyst and diffusion layer can be assessed. The losses determined by this technic are the Ohmic, mass transport and activation. With this technic flooding and dry can be isolated and degradation studies can be made. Finally, this technic can be applied to a real system were this data can be used to improve control strategies for performance and durability when integrated in to a model based controller.

Keywords: Tafel slope, mass transport, Ohmic resistance, voltage losses, diagnosis

1 Introduction

Since the first PEMFCs (Polymer Electrolyte Membrane Fuel Cell) developed in the late 1950s there has been a remarkable technological progress towards increasing their efficiency and reducing the platinum loading, through the development of new membranes and electro-catalytic nanoparticles and the improvement of the electrode structure thanks to the growing fundamental understanding in modern material and porous media science. Even if the overall operating principle of a single cell remains relatively simple, complex mechanisms at different spatial scales strongly interplay during the PEMFC operation limiting the effectiveness of the catalyst activity. In fact, processes at the smaller scales, e.g. Oxygen Reduction Reaction (ORR) on the cathode platinum nanoparticles, dominate the processes at the larger scales (e.g. liquid water transport through the cathode carbon support) which in turn affect the processes at the smaller scales, e.g. through the water flooding limiting O₂ transport in the cathode or drying and limiting the proton conductivity in the catalyst layer. It is extremely important for most applications to accurately predict PEMFC state-of-health to improve efficiency and durability. For that purpose, it is necessary to develop diagnostic schemes that can evaluate PEMFC state-of-health adequately.

In order to achieve this, several steps are required:

- to understand the interplay between individual scales over the spatiotemporal hierarchies with their possible competitive or synergetic behavior;
- to identify the contribution of each mechanism into the global cell response under dynamic conditions;
- to design separated controllers for an online control of the PEMFC behavior to enhance its durability under specific operation conditions (e.g. by controlling the dynamics of the reactants flow, rela-

tive humidity, temperature, pressure etc.).

In this context this paper is dedicated to the experimental implementation of a state-of-health diagnostics process to determine the major polarization losses in a single cell. Specifically determine the Ohmic, mass transport, and activation losses.

2 Experimental

The operating conditions of the tests are described in table 1.

Table 1. Fuel Cell operating conditions

Set point	Units	Value
Anode pressure	bar	1.25
Cathode pressure	bar	1.23
Anode RH	%	50
Cathode RH	%	30
Anode stoichiometry	-	1.3
Cathode stoichiometry	-	1.3, 1.5, 2.0
FC Temperature	°C	60, 80
Line heater Temperature	°C	65, 85

What has to be mentioned is that these values, except for stoichiometry, can vary during the fuel cell test, but not that significantly to affect the fuel cell performance. Calculations with the experimental data have been done to ensure this.

2.1 Polarization Curve

The purpose of the Polarization Curve (PC) is to obtain the steady state voltage output of the fuel cell. Current and voltage are measured during 180 seconds in order to get an i-V curve that shows the progressive losses of the fuel cell. These results will be compared with the fast Current Sweep (CS) (in the order of 2 seconds). The aim is to see the difference since with the PC all the parameters are changing, affecting the fuel cell performance, while with the fast analysis the internal parameters don't change. For the PC between 22 and 24 points are obtained, depending on the maximum current sup-

ported by the fuel cell at the defined conditions. Two different temperatures 60°C and 80°C, and for every temperature three different cathode stoichiometry 2.0, 1.5 and 1.3 are tested.

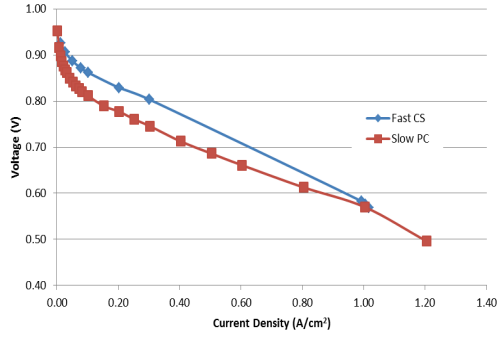


Fig. 1. Experimental Polarization Curve compared to a fast current Sweep at 80°C, cathode's stoichiometry of 2.0 and 1 A/cm² (25 Amps).

2.2 Electrical Impedance Spectroscopy

The Electrical Impedance Spectroscopy (EIS) consists in sending AC signals through a frequency spectrum (between 0.05 and 2000 Hz) to obtain a Nyquist diagram that shows the impedance of the fuel cell at various frequencies. The Nyquist only gives linear information at the measured point of operation: at low frequencies real axis intercept we have the total resistance $Z=R_{tot}$, whereas at high frequency real axis intercept we have the Ohmic resistance $Z=R_{Ohm}$. In this study only the high frequency resistances are used to calculate the Ohmic losses of the fuel cell.

2.3 Current Sweep

The purpose of the current sweep is to obtain an i-V curve of the fuel cell where the internal conditions are constant throughout i.e. that water in catalyst, membrane and diffusion layers. The currents sweep consists of points obtained by quickly passing through specifically selected current set points.

As can be seen in Fig. 2 there are 10 current rest points, 3 points with a difference to the operating current of 0.3 A and 7 points in the nonlinear region at lower current densities. The points around the operating condition give a good reading of the linear slope of the fuel cell i.e. the total resistance. The others, at low current densities give a good reading on the nonlinear region of the fuel cell.

In this study the fuel cell is left at each current set point for only 200 ms, which mostly provides enough time for the electrochemical part of the fuel cell to stable out.

Currents sweeps have been done for 60°C and 80°C, at the three cathode's stoichiometry's, starting at three steady state current densities (0.2, 0.5 and 1 A/cm²), as can be seen in Fig.3.

Figure 3. explains the whole test routine, starting with the polarization curve until arrive to the 1 A/cm², once the system is stable at this current,

EIS and CS are done at each current density with a rest time after each step as shown in figure 3.

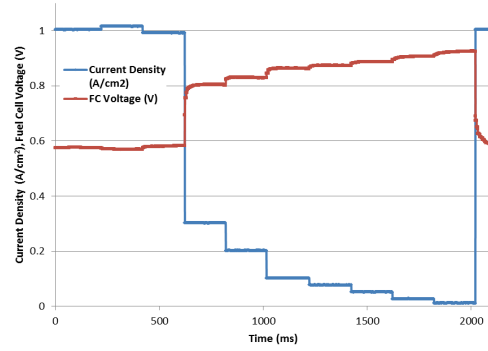


Fig. 2. Experimental current Sweep at 80°C, cathode's stoichiometry at 2 and 1 A/cm² (25 Amps).

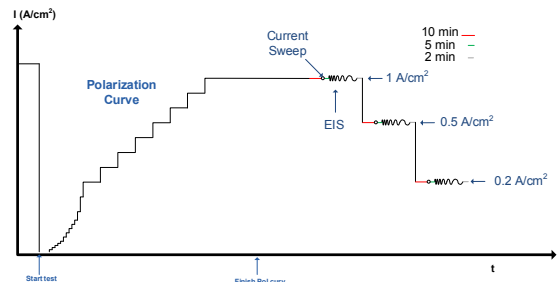


Fig. 3. Scheme of the tests, starting with the polarization curve and then the currents sweeps and the EIS at each current density.

To obtain the data for the current sweep it is only needed to recover the i-V value of each of these 10 points after they are stable, resulting what is shown in Fig.1 under Fast CS.

The following steps to obtain the voltage losses of the PEMFC have been already described in [1], knowing that the theoretical voltage of a fuel cell is [3]:

$$V_{fc} = E_{(T,P)} - \Delta V_{act} - \Delta V_{mt} - \Delta V_{ohm} [V] \quad (1)$$

This decomposition is explained graphically in figure 4. Where we can see all the elements of equation 1, and the calculation will be explained throughout this text.

First of all the calculation of the theoretical Open Circuit Voltage (OCV) of the fuel cell considering different temperatures and pressure of the anode and the cathode is calculated [2]:

$$E_{T,P} = - \left(\frac{\Delta H^0}{nF} - \frac{T\Delta S^0}{nF} \right) + \frac{RT}{nF} \ln \left[\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}} \right] [V] \quad (2)$$

Where ΔH^0 is the change in enthalpy and ΔS^0 is the change in entropy of the reaction at standard conditions, which are considered to be 25°C and 1 atm. The values at these conditions are, respectively, -285826 J/mol and -163 J/mol/K. n represents the number of electrons transferred per mole, which in this case is 2 for H₂, F is Faraday's constant (96485.4 J/V/mol) and R is the universal gas

constant (8.314472 J/molK). The partial pressures have been calculated with the data from the relative humidity of the anode and cathode and depending on the temperature.

The theoretical OCV of the FC is 1.187 V at 60°C and 1.167 V at 80°C.

Having the theoretical value of the fuel cell voltage and the real value, from the CS it is possible to calculate the activation losses, the Ohmic losses and the mass transport losses.

First of all with the R_{Ohm} value obtained from the EIS it is possible to calculate the Ohmic losses of the fuel cell by applying Ohms law:

$$V_{Ohm} = iR_{Ohm} \quad (3)$$

Where I is the current (A/cm^2) from the 10 stable points of the CS and R is the relative resistance (Ωcm^2).

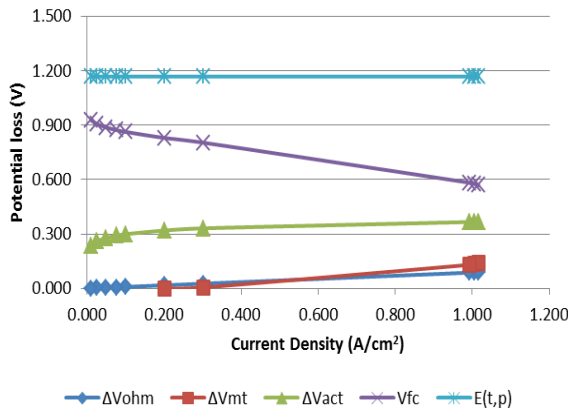


Fig. 4. Voltage losses of the FC 80°C, cathode's stoichiometry at 2 and 1 A/cm^2 (25 Amps).

Subtracting the Ohmic losses from the total losses the result is a curve that contains the activation losses and the mass transport losses. Now, assuming that in the nonlinear region of the curve [1] their are only activation losses which are the 7 points at the low current densities. Finally, the mass transport losses are the result of subtracting the activation losses and the Ohmic losses from original curve.

From these curves it is possible to obtain the indicators R_{mt} (Mass Transport relative resistance) and the Tafel Slope. R_{mt} is simply the slope of the linearization of the V_{mt} obtained before. The Tafel Slope is the slope of the linear part of the logarithmic linealization of the activation losses curve.

3 Results

As a result from the whole process, graphs of the voltage losses and their corresponding indicators are presented below.

The voltage losses are presented only for the operating point ($1 A/cm^2$), while the indicators are represented for the three different current densities.

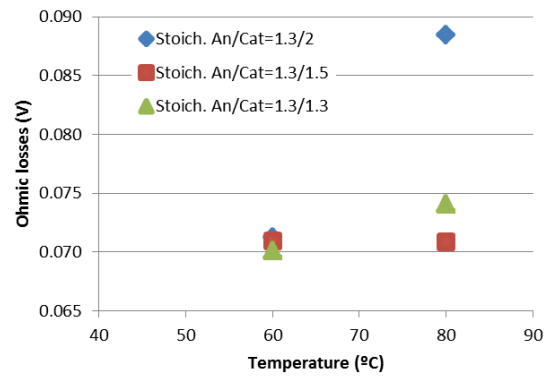


Fig. 5. Ohmic losses at 1 A/cm^2 with respect to stoichiometry and temperature.

The Ohmic losses are the lowest in all cases, always below the 0.1 V at the operating point. Even if they get higher with the temperature, this variation is very small.

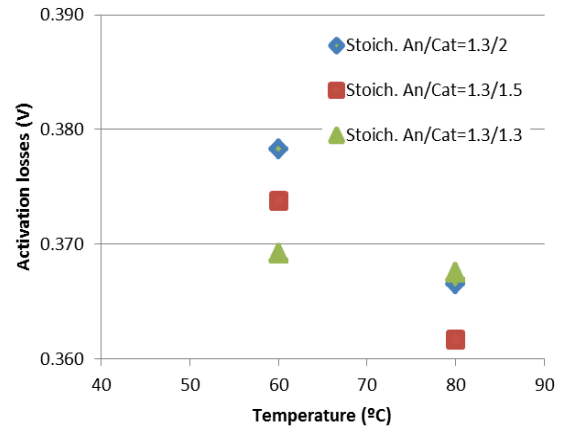


Fig. 6. Activation losses at 1 A/cm^2 with respect to stoichiometry and temperature.

The activation losses are the highest. They are followed by the mass transport losses that vary mainly due to stoichiometry, while the activation losses don't vary much with respect to stoichiometry. However with temperature increase, the activation losses decrease. The same occurs with the mass transport losses, even though the variation is much larger than that for the activation losses. The range of the mass transport losses is between 0.1 V and 0.35 V (in this temperature range), while for the activation losses the range is between 0.36 V and 0.38 V.

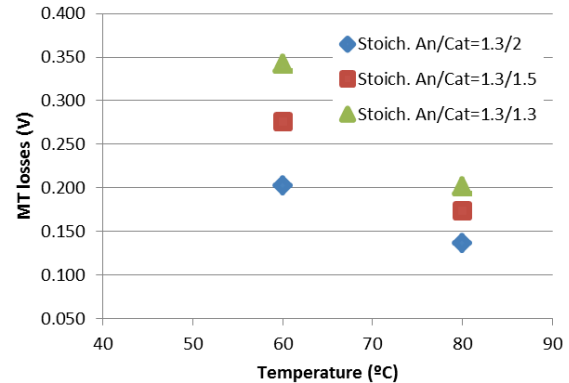


Fig. 7. Mass transport losses at 1 A/cm² with respect to stoichiometry and temperature.

According to the indicators graphs are in line with the voltage losses results, the Ohmic resistance is higher at higher temperatures and for higher cathode stoichiometry. What can be seen is that this indicator decreases with higher current densities, even if it stays between 0.07 Ωcm² and 0.08 Ωcm².

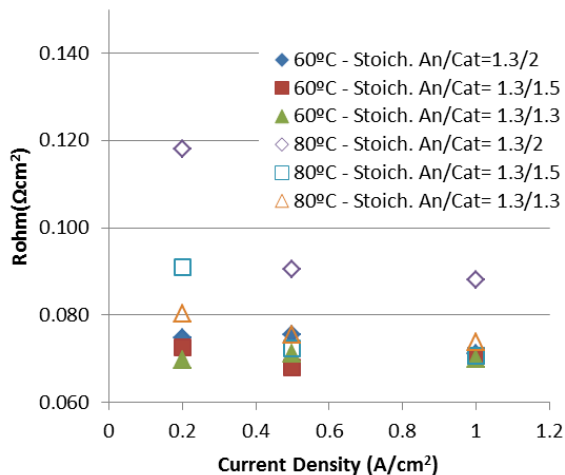


Fig. 8. Ohmic resistance as the Ohmic indicator, respect stoichiometry and current density.

The Tafel Slope depends on the current density: the higher the current density, the lower the Tafel slope. The dependency on temperature or stoichiometry is not that important: for each current density, the indicators at different temperatures and stoichiometries are in an order of 0.015.

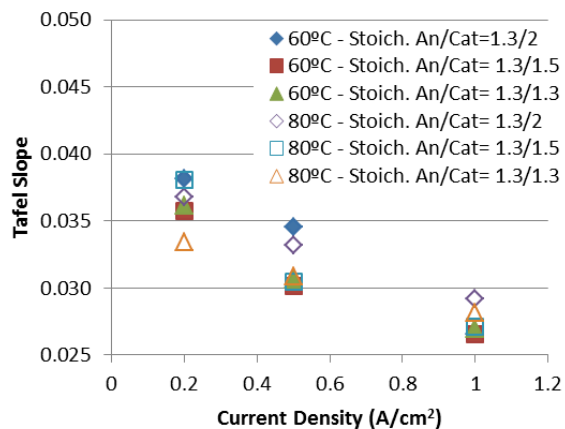


Fig. 9. Tafel slope as activation indicator, respect stoichiometry and current density.

The mass transport indicator (represented as a resistance) is higher for higher current densities. Also the higher the temperature, the lower the indicator. According to the stoichiometry, for lower values of the cathode stoichiometry, this indicator is bigger (specially for the stoichiometry 1.3).

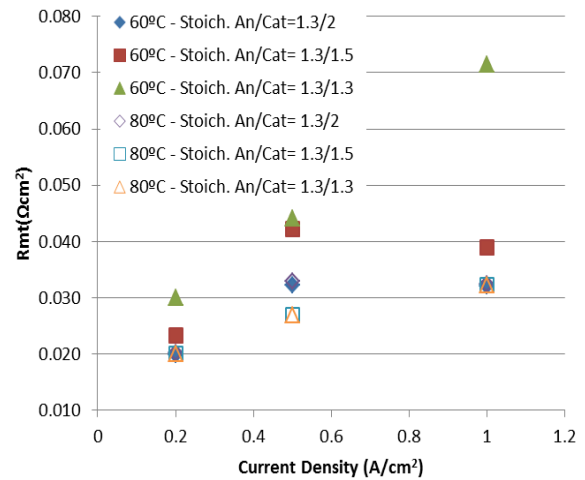


Fig. 10. Linear mass transport indicator represented as a resistance, with respect to stoichiometry and current density.

4 Conclusions

The decoupling of the current sweep with the Ohmic resistance is a very powerful tool to determine the cause of the losses inside of a fuel cell. In a time frame of seconds, the fuel cell can be diagnosed and critical information on the state of the membrane, catalyst and diffusion layer can be assessed. With this technic flooding and dry can be isolated and degradation studies can be made. Finally, this technic can be applied to a real system were this data can be used to improve control strategies for performance and durability improvements.

5 Acknowledgements

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6 References

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