

Experimental Characterization and Identification of the Voltage Losses in an Open Cathode PEM Fuel Cell Stack

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1 Introduction

For the past 20 years remarkable progress has been made in PEM fuel cell materials, component design, production, and system power density improvements. However, there is still a lot to be done in the field of fuel cell system control, which makes it essential to understand the different physical phenomena within a working fuel cell and how they need to be controlled in order to improve efficiency, operating range and durability. This experimental study analyses the effects of ambient conditions, through the use of an environmental chamber, on a Horizon® H-100 20 cell stack, 22cm² active area, open cathode, where the only active control mechanism employed is a single fan that both, cools and provides the oxygen needed for the reaction. All the other control mechanisms are disconnected and a constant dry pure hydrogen flow rate of 1.8 SLPM is supplied to the stack.

The objective is to isolate and determine the different voltage losses with respect to the ambient conditions and currents.

2 Fuel Cell Voltage Losses Model

The thermodynamic reversible potential of a PEM fuel cell can be defined as:

$$E_{(T,P)} = \frac{\Delta G^0}{nF} + \frac{\Delta \hat{s}}{nF} (T - T_0) - \frac{RT}{nF} \ln \left(\frac{\prod a_{prod}^{v_i}}{\prod a_{react}^{v_i}} \right) \quad (1)$$

where ΔG^0 is the Gibbs free energy at standard temperature and pressure (which in this study is considered to be 25°C and 1 Atm). n is 2, the number electrons transferred per mole, F is Faraday's constant and R is the universal gas constant. $\Delta \hat{s}$ is the entropy change of the reaction and is assumed to be constant in the temperature range of the fuel cell. T and T_0 are the operating and standard temperatures, respectively. a_{prod} and a_{react} are the activities (or concentrations) and v_i is the corresponding stoichiometric coefficient of each species participating in the reaction (which is 1 for all the species except for O_2 where $v_{O_2} = 1/2$) [O'Hayre 2009].

When the fuel cell is not connected to an external circuit, the fuel cell voltage would be expected to be close to the thermodynamic potential, relative

to the ambient conditions and reactant concentrations. However, the measured fuel cell voltage is much lower, usually less than 1V/cell, which can be attributed to hydrogen crossover and internal currents. As a load is applied to the fuel cell, the voltage drops further. The three major unavoidable voltage losses determined in this study are activation, mass transport and ohmic losses [Larminie & Dicks 2003]. So, the fuel cell voltage can be expressed as:

$$V_{(fc)} = E_{(T,P)} - \Delta V_{act} - \Delta V_{imp} - \Delta V_{ohm} \quad (2)$$

2.1 Activation polarization losses:

A certain proportion of the energy is needed to start the chemical reaction, this phenomena produces a non-linear voltage drop, called activation polarization losses. These losses occur on both anode and cathode catalysts. However, the reduction of oxygen is a much slower reaction than the oxidation of hydrogen, and therefore the reduction reaction produces larger activation polarization losses, thus the anode side losses are neglected. The voltage losses due to activation polarization can then be described as [Barbir 2005]:

$$\Delta V_{act} = \frac{RT}{\alpha nF} \ln \left(\frac{i}{i_0} \right) \quad (3)$$

The parameter α is the charge transfer coefficient and expresses how the change in the electrical potential across the reaction interface changes the reaction rate. It depends on the type of reaction and the electrode material. Its value is theoretically between 0 and 1 [Larminie & Dicks 2003]. The exchange current density i_0 is the rate at which the reaction proceeds (simultaneously in both directions) at equilibrium potential $E_{(T,P)}$, when the net current equals zero [Barbir 2005]. The fuel cell current density is denoted by i . The activation losses are generally the dominant effect on the fuel cell voltage, as is shown in figure 1.

Although the membrane in a PEM fuel cell is not electrically conductive and is impermeable to gases, a certain amount of hydrogen diffusion and electron transport through the membrane is possible. These internal current losses are considered to compute the crossover losses (ΔV_{cros}).

$$\Delta V_{cros} = \frac{RT}{\alpha nF} \ln \left(\frac{i+i_{loss}}{i_0} \right) \quad (4)$$

Where i_{loss} takes into account the total hydrogen

crossover and the internal current losses. In this study these losses are considered part of the activation losses. [Barbir 2005]

2.2 Ohmic losses:

The resistance to the flow of electrons through the electrically conductive fuel cell components and to the flow of ions through the membrane causes a voltage drop, which can be expressed by Ohm's law:

$$\Delta V_{ohm} = i \cdot R_{ohm} \quad (5)$$

The internal cell resistance R_{ohm} is in [Ωcm^2], where the electric and contact resistance can be considered constant. The ionic resistance changes depending on water concentration in the membrane.

2.3 Mass transport losses:

The consumption of reactant gases at the electrodes leads to concentration gradients and thus changes in the partial pressure of the reactants, which affect the fuel cell voltage as seen previously in equation (1). Referring to Faraday's laws of electrolysis, the transferred charge and the molar flux of a reactant J are proportional to the current density [Barbir 2005]:

$$J = \frac{i}{nF} \quad [mol \ s^{-1} m^{-2}] \quad (6)$$

The higher the current density, the lower the reactant concentration is at the catalyst layer.

The current density at which the reactant concentration reaches zero is called the limiting current density i_L . Considering this relationship between reactant mass transport and current density, the mass transport polarization losses can be expressed as [Barbir 2005].

$$\Delta V_{conc} = \frac{RT}{\alpha nF} \ln \left(\frac{i_L}{i_L - i} \right) \quad (7)$$

Since this study only considers the linear region of the fuel cell the mass transport losses can be assumed to be linear. So equation (7) can be considered using Ohm's law:

$$\Delta V_{conc} = i \cdot R_{imp} = \Delta V_{imp} \quad (8)$$

assuming that the major portion of the impedance is due to mass transport resistance [Barbir 2005].

3 Experimental Approach

The following experimental approach is used to isolate the individual losses in the fuel cell stack.

3.1 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is performed at steady state conditions with amplitude of 5% of the current set point and a frequency range of 0.1 Hz to 10,000 Hz. The main purpose of this test is to determine the high and low frequency resistances in a Nyquist plot. The high frequency real axis intercept is considered to be the ohmic resistance (R_{ohm}) in equation (5) and the low fre-

quency real axis intercept is the total resistance of the fuel cell. The ohmic subtracted from the total gives the impedance of the system, which is mainly considered to be the sum of linear activation and mass transport resistances. Due to this it is very difficult to isolate the mass transport from activation impedance losses. Thus it is assumed that in the linear region of the fuel cell polarization curve, the main contribution to impedance is due to mass transport resistance [Barbir 2005].

$$R_{imp} = R_{total} - R_{ohm} \quad (9)$$

The Nyquist plot only gives information about operating current at which it is measured. Therefore the activation losses need to be determined from another method. In this study this was done by data extrapolation from a current sweep, as explained in section 3.2.

3.2 Current sweep

The purpose of current sweeps is to obtain a polarization curve of the fuel cell with minimal changes to the internal conditions. Once the fuel cell has reached steady state conditions, a current sweep is performed. The time constant of the system is determined from the EIS ($\tau = 0.6ms$). Thus the fuel cell is left at each current set point for only 0.6 seconds which is approximately $10 \times \tau$. The rest time at each set point has to be kept to a minimum due to the nature of the open cathode system where the water content and the temperature in the fuel cell are driven by the current. Then from this sweep the total measured resistance from the Nyquist plot is added to the fuel cell and a new curve is plotted that represents the activation polarization as shown in figure 1 from experimental data. This assumes that during a quick sweep the resistances from the Nyquist are still valid due to the minimal change to the internal conditions in the stack.

3.3 Breakdown of the current sweep

Using equation (1) to calculate the reversible fuel cell potential and then subtracting out the total losses, $i \cdot R_{total}$, gives the activation losses of the fuel cell. Then using only the data in the non-linear section (from 0 to 0.05 A/cm²) an equation for the natural logarithmic of the data can be extracted and used in the Tafel equation (10) to determine the i_0 and α .

$$\Delta V_{act} = -\frac{RT}{\alpha nF} \ln(i_0) + \frac{RT}{\alpha nF} \ln(i) \quad (10)$$

3.4 Ambient & operating conditions

The ambient conditions set in the environmental chamber were 20°C with 98%RH, 30°C with 55%RH, and 30°C with 25%RH. The combined cathode and cooling fan was set with a constant fan flow rate of 70% power. Anode flow rate was 1.8 SLPM of pure dry hydrogen. The current set points for the sweep were 0.002, 0.006, 0.011, 0.015, 0.024, 0.046, 0.068, 0.090, and 0.222 A/cm² with a settling time of 0.6 at each set point.

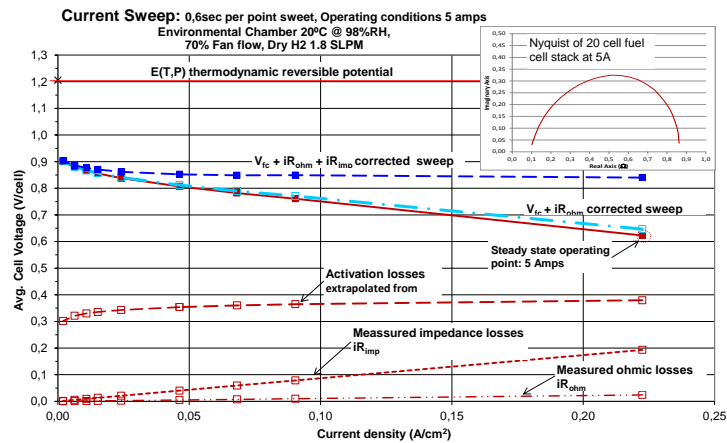


Fig. 1. Dissection of a real current sweep to determine the activation polarization

4 Results and Discussion

In this section several results are discussed, with respect to current, ambient temperature and ambient relative humidity.

Current seems to be the main influence on the fuel cell voltage by affecting the activation polarization as shown in figure 4. There seems to be little effect on the membrane resistance or the mass transport resistance in this fuel cell stack as shown in figure 3. From the data analyse, both α and i_0 change with changes in current. However looking just at the linear portion of the fuel cell current sweep α seems to be linear and with a constant slope and its y axis intercept affected more by ambient relative humidity and then by ambient temperature as seen in figure 2a. i_0 also seems to have a constant slope in a logarithmic scale but the y axis intercept does seem to be effected by both ambient temperature and relative humidity as shown in figure 2b. It is important to note that the control objective will be to maximize both α and i_0 .

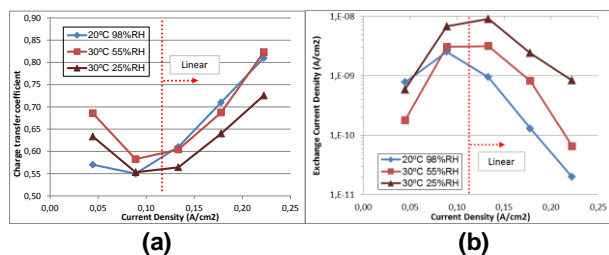


Fig. 2. Environmental chamber set point of 20°C and 30°C with relative humidity of 98%, 55% and 25%. (a) Charge transfer coefficient with respect to current density. (b) Exchange current density with respect to current density.

It is interesting to note that α in figure 2a decreases with lower ambient relative humidity while i_0 increases and the fuel cell voltage is slightly lower with a low ambient relative humidity.

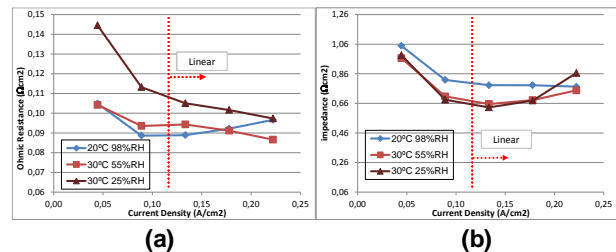


Fig. 3. Environmental chamber set point of 20°C and 30°C with relative humidity of 98%, 55% and 25%. (a) Ohmic resistance with respect to current density. (b) Impedance with respect to current density.

This indicates that the change in α had the greater effect on the fuel cell voltage. Taking into consideration that membrane resistance and the impedance are practically identical.

5 Conclusions

Using this technic to isolate the different voltage losses seems to work quite well. Through the data analyses it is clear that the major objective of the controller will be to minimizing the activation polarization by maximizing both α and i_0 . Future work will be dedicated to determining how the fan flow rate and the hydrogen purge in an open cathode system influence the activation polarization and how the important parameters will be monitored online.

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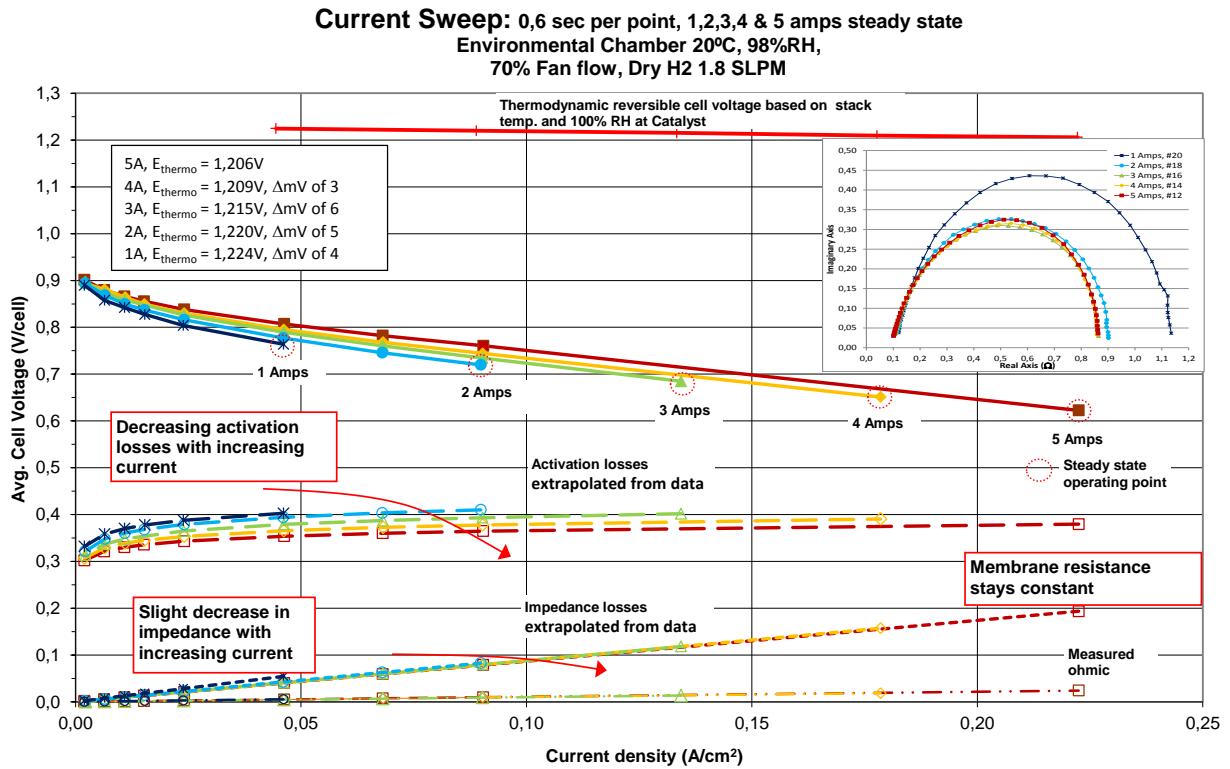


Fig. 4. Environmental chamber set point of 20°C and 98% RH. Current sweeps and EIS done when fuel cell has reached steady state for the different current set points.

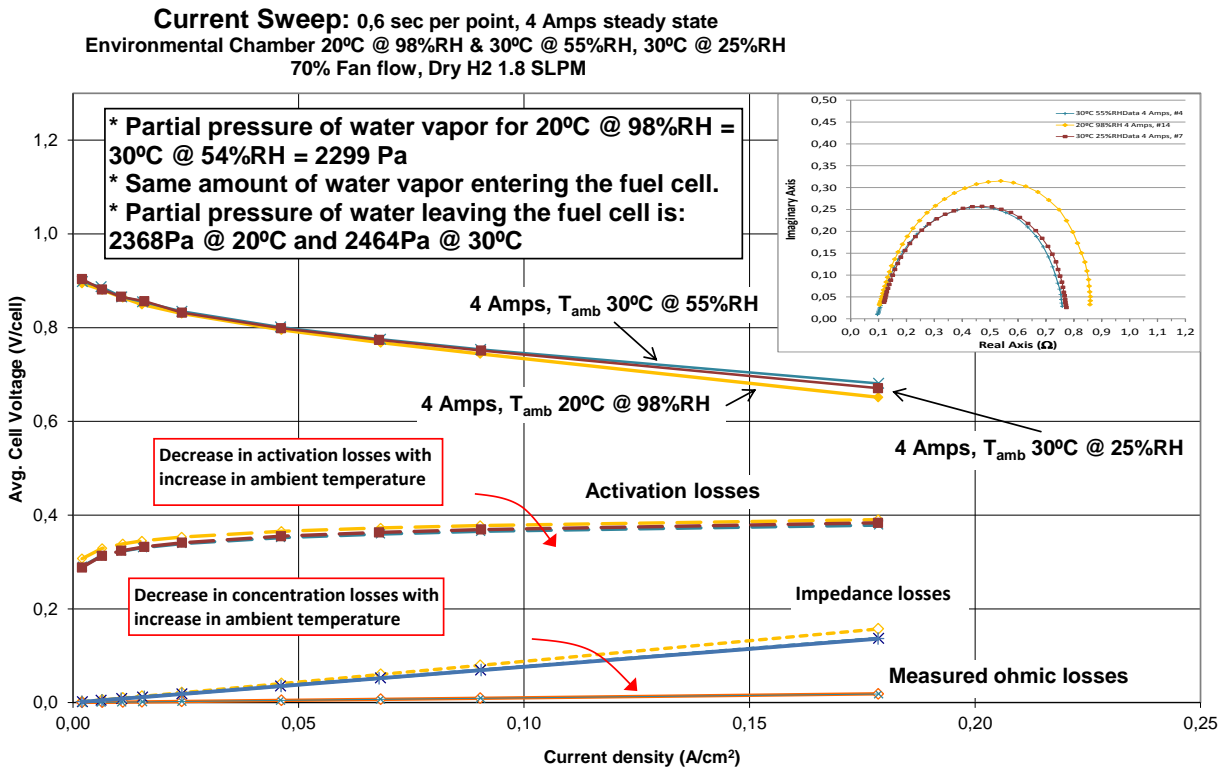


Fig. 5. Environmental chamber set point of 20°C and 98% RH, 30°C and 55% RH and 20°C and 25% RH. Current sweeps and EIS done when fuel cell has reached steady state for the different current set points.

7 References

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