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Advanced Fuel Cell Diagnostic Techniques for Measuring MEA Resistance

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Overview

Of the fuel cells available, the proton exchange membrane (PEM) type is the subject of much research in recent years due to its high efficiency, ruggedness, and low-temperature operation. The central component of the PEM fuel cell is the membrane-electrode assembly (MEA), consisting of a microporous ion transport membrane coated with catalysts and conductive materials. This article examines and compares presently available methods for measuring MEA resistance, an important metric of PEM fuel cell performance, as well as the resulting data from these methods.

The fuel cell can be modeled by the equivalent circuit shown in Figure 1. This is a simplified version of the Randles equivalent circuit, a model commonly applied to electrochemical systems in which contact resistance and other effects are small enough to ignore. In the case of the fuel cell, the cathode polarization resistance is much larger than that of the anode, so this circuit model omits the anode elements. Polarization Resistance is the reaction equivalent, Double-Layer Capacitance is the interfacial capacitance of the cathode, and Membrane Resistance (the MEA resistance for a PEM fuel cell) is the resistive loss of the polymer electrolyte (membrane) to be measured. The Voltage Source element is an ideal DC voltage source (zero internal impedance, constant voltage) with a potential equal to the open-circuit voltage of the fuel cell. This element does not affect AC analysis but allows the model to approximate the DC behavior of the fuel cell.

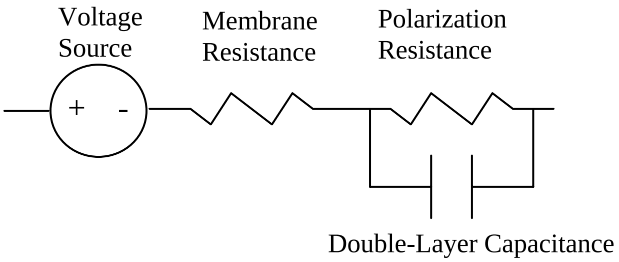


Figure 1 – Simplified Equivalent Circuit for PEM Fuel Cells

Note that the values of these equivalent circuit components are a function of the cell's operating current or voltage, making the fuel cell an electrically nonlinear device. The sum of the membrane and polarization resistances can be determined from the slope of the DC voltage-current characteristic curve (polarization curve) of the cell. The membrane resistance is a particularly important measure of single fuel cell (or fuel cell stack) electrical performance since it quantifies internal cell losses. It is desirable to monitor membrane resistance during membrane development and subsequent manufacture of stacks, since ohmic losses generate waste heat that must be removed from the fuel cell, resulting in a decrease in overall electrical efficiency. Since fuel cell current densities are quite high when compared to other electrochemical processes, even small amounts of ohmic resistance (milliohms) have a significant effect on overall efficiency. Unfortunately, while the ohmic resistance of some fuel cell components can be measured when disassembled, membrane resistance cannot be directly measured by conventional DC methods when installed in a fuel cell. Since the MEA is a solid electrolyte ion transport path, effective resistivity may be dependent on hydration and many other factors. In addition, DC methods cannot isolate membrane resistance from polarization resistance.

Fortunately, the electrode / solid electrolyte interface has a large capacitance associated with it (Double-Layer Capacitance in Figure 1) that allows an AC measurement to be used to determine the membrane resistance separately from the polarization resistance. This may be performed several different ways, but all have some common traits:

1. All methods impose a changing electrical condition on the fuel cell.
2. All methods measure current or voltage waveforms resulting from that change.
3. All methods require an accurate voltage measurement directly at the cell terminals using a four-terminal (Kelvin) method.

Current Interrupt Method

This time-domain AC technique, developed over 50 years ago, quickly interrupts the fuel cell current and rapidly measures the terminal voltage before and during the interruption. Since the cell voltage is a combination of the charged anode and cathode potentials less the resistive drop of the membrane, the cell voltage rises by the amount of the drop across the membrane resistance. By comparing the -pre and –post interrupt voltage and dividing the difference by the current, the membrane resistance may be determined. Advantages of this method include a single data value which is easily interpreted and no need for external equipment. Disadvantages include limited information given since it is only one data value and degraded operation if long cell cables are used, due to ‘ringing’ caused by cable inductance. Example voltage and current are shown in Figure 2.

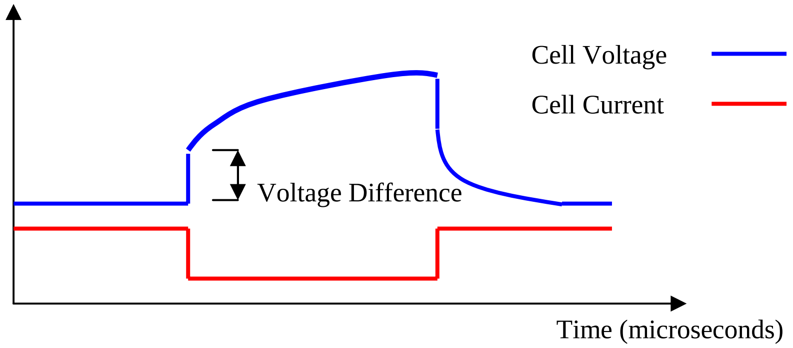


Figure 2 – Typical Current Interrupt Waveform

AC Resistance Method

This method uses an AC resistance measurement device, such as an external AC milliohm meter, to apply a fixed, single high frequency sine wave (typically ~1 KHz) to the fuel cell under test to measure the total impedance magnitude of the cell and the load in parallel at that frequency. The high-frequency zero-phase point should yield the membrane resistance. The data must then be corrected for the parallel load impedance to determine the actual ohmic resistance of the membrane.

Like the current interrupt, this method only provides a single data point, which can be an advantage or disadvantage. An advantage is that the cell is minimally disturbed electrochemically by the measurement, but unfortunately accurate results cannot be obtained without exact gain-phase characterization of the impedance of the electronic load at the operating conditions of the test (DC voltage, DC current, frequency) using external frequency-analysis equipment. Additionally, the zero-phase condition of the load-cell combination measured by the milliohmmeter is not meaningful since it is not the zero-phase impedance of the cell (the load has a complex impedance in parallel with the complex impedance of the cell). The only way to separate the actual cell impedance is to use the measured load impedance and reported magnitude and phase data of the milliohmmeter to calculate the impedance of the cell itself. These difficulties stem from the millohmmeter not being intended to measure energy sources under load.

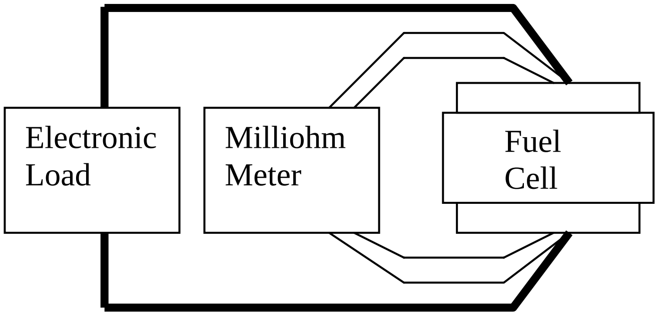


Figure 3 – AC Resistance Measurement Technique

Electrochemical Impedance Method

This technique involves applying a small amplitude AC current perturbation through the electronic load on the larger DC cell current. The resulting variations in cell voltage and current magnitude and phase are sent to a frequency response analyzer to determine the complex impedance of the cell under test. The frequency of the applied signal may be swept over a range (typically 10kHz to 1Hz or lower), producing a rich data set from which several parameters may be extracted. The amplitude and phase of the signals may be plotted in Bode and Nyquist formats for analysis and modeling. This method may be used to determine MEA resistance as well as provide information about kinetics and mass transport within the fuel cell.

Unlike the current interrupt and AC resistance methods, electrochemical impedance measurement provides the advantage of a large amount of useful information about the cell. An advantage is that, like the AC resistance method, the cell under test is minimally disturbed and therefore not electrochemically changed by the measurement.

Modeling software is available to allow accurate analysis of the electrical and reaction characteristics of the fuel cell. Disadvantages include a need to interpret the large amount of data produced and the additional cost of the required equipment.

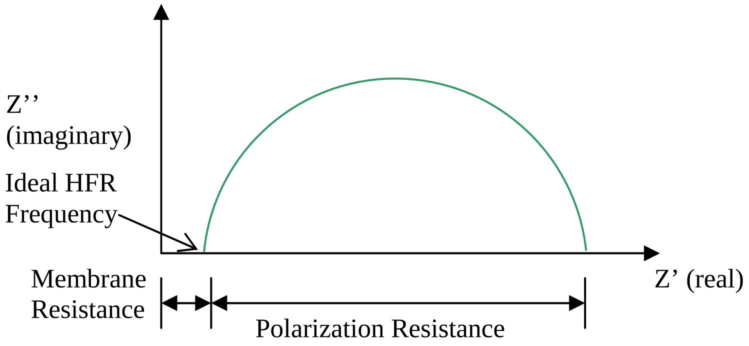


Figure 4 – Nyquist Plot of Fuel Cell Impedance

High Frequency Resistance Method

The High Frequency Resistance (HFR) method is actually a subset of the Electrochemical Impedance Method described earlier. An AC signal is applied to the electronic load to modulate the DC load current and the voltage and current AC response is measured by a frequency response analyzer. Unlike the Electrochemical Impedance Method, however, only a single frequency is used. This measurement is automatically performed periodically during normal test system operation and the result displayed in real time. Usually the Real (Z') component of the result is of interest and is displayed in milliohms.

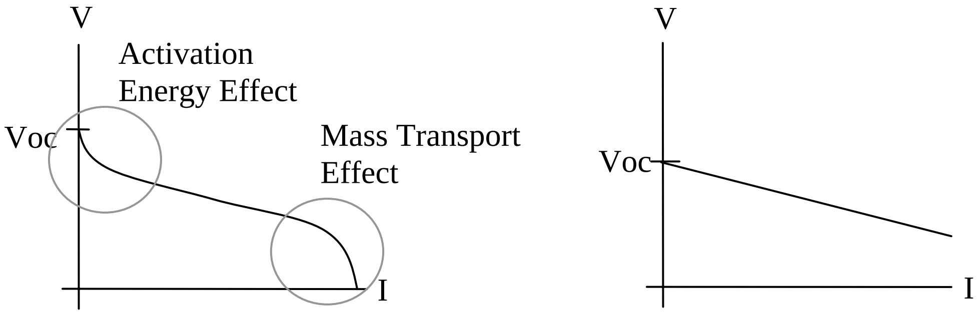
The measurement frequency used for this technique must be selected with care. It should ideally be the frequency at which the Nyquist plot of Figure 4 crosses the real axis at the high frequency (low Z' or Real Z) point. If the Nyquist plot doesn't cross the Real axis at high frequency, the highest frequency before the plot deviates from the semicircular shape may be used or the intercept of the data fit to a semicircle or other model may be used. Typical HFR measurement frequencies range from 500Hz to 3kHz. In any case, the same frequency must be used for data comparisons to be valid.

Note that the method for choosing the HFR frequency requires that the test system also have Electrochemical Impedance capability. This is not a problem because a true frequency response analyzer can measure over a wide range of frequencies, so a test system capable of true HFR measurement will also be capable of performing Electrochemical Impedance measurements.

Comparison of Techniques

The objective here for each of these methods is to determine the membrane resistance of the fuel cell.

The two techniques which are most easily compared are the Current Interrupt and HFR methods. The Current Interrupt result usually correlates well with the HFR data if the measurement frequency is properly chosen as described in the HFR section. There is, however, usually some difference. This is explained by the nature of the two methods; one applies a large signal and looks at time domain response while the other applies a small signal and uses the frequency domain response. If an actual fuel cell behaved like an ideal voltage source (zero source impedance) in series with the equivalent circuit of Figure 1, the results of the two methods would be identical. Unfortunately, the fuel cell exhibits significant nonlinear large-signal behavior, as shown in Figure 5a due to activation energy and mass transport effects. The polarization curve of the equivalent circuit shown in Figure 1 would look like that of Figure 5b if there was no nonlinear behavior.



5a

Fuel Cell Polarization Curve (typical)

5b

Dummy Cell Polarization Curve

Figure 5 – Comparison of Equivalent Circuit Polarization Curve to Actual Fuel Cell

In practice, the results from Current Interrupt and HFR techniques are usually similar because the polarization curve is nearly linear over the middle-current operating range of the fuel cell typically used, particularly if cell current is not sufficient to enter the mass transport effect region.

The Electrochemical Impedance method, as described earlier, produces a complete spectrum of data, a superset of that from the HFR method. The data point at the frequency chosen for HFR measurement should have the same Real (Z’) value as the data produced by the HFR measurement.

The data from the AC Resistance method is not directly comparable to that produced by the other methods due to the artifacts imposed by the parallel-connected electronic load, as described earlier.

Conclusion

Each of these methods may be used to determine the resistance of the fuel cell membrane, and in the impedance case, valuable information about other cell parameters. The user should understand how to properly apply and interpret the data from each of these techniques if useful measurement of cell performance is to be obtained.

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