Electrical Test Methods for Evaluating Fuel Cell MEA Resistance

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During the past few years, fuel cell developers have moved rapidly toward a commercially viable product that is now being introduced into the marketplace. Today, one of the most promising fuel cell types is the proton exchange membrane (PEM) cell. As the membrane-electrode assembly (MEA), the active component of the PEM fuel cell, begins to reach production in moderate quantities, there have been many performance-improving changes such as thinner membrane materials for improved ion transport and faster hydration. Along with these developments, there exists a need for accurate, meaningful measures of fuel cell performance, especially of membrane resistance. Several methods have been developed and will described here.

The fuel cell, like other electrochemical cells, can be modeled as an equivalent electrical circuit. The Randles circuit, shown in Figure 1, is a simple model commonly applied to electrochemical systems in which contact resistance and other effects are small enough to ignore.

The Randles circuit models the behavior of the anode and cathode electrochemical reactions

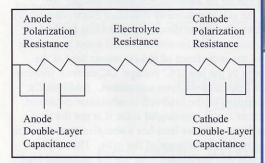


Figure I. Electrochemical Equivalent Randles Circuit

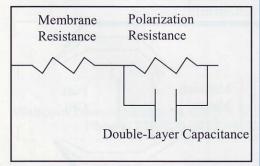


Figure 2. Simplified Equivalent Circuit for PEM Fuel Cells

as well as the electrolyte itself. In the case of the fuel cell, the cathode polarization resistance is much larger than that of the anode. Therefore, the fuel cell may be represented in some cases by a circuit model omitting the anode elements. The resulting simplified equivalent circuit is shown in Figure 2. Polarization Resistance is

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the reaction equivalent, double-layer capacitance is the interfacial capacitance of the cathode, and membrane resistance (the electrolyte resistance for a PEM fuel cell) is

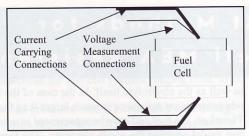


Figure 3. Four-Terminal Measurement

the resistive loss of the polymer electrolyte to be measured. The values of these equivalent circuit components are a function of the cell's operating current or voltage.

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 cell and stack 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 2) that allows an AC measurement to be used to determine the membrane resistance separately from the polarization resistance. This has been performed in several different ways, but all have some common traits:

- 1. All methods impose a changing electrical condition on the fuel cell.
- 2. All methods require an accurate voltage measurement directly at the cell terminals.

The four-terminal method, shown in Figure 3, requires a current flow through the circuit or material to be evaluated, and measurement of the resulting voltage drop over the whole or partial length of the circuit or material under test. This requires four electrical connections - the two "outside" connections carrying the current and the two "inside" connections measuring the voltage drop in the material or device through which the current is flowing. The four-terminal method avoids the error of contact resistance and wiring in the measurement circuit, since the current carrying and voltage measurement connections are independent.

Current Interrupt Method - developed over 50 years ago, this method involves an instantaneous interruption of the fuel cell current and the rapid measurement of the terminal voltage before and after the interruption. Although current interrupt measurement may seem to be a DC technique, it actually involves measurement of transient response to an input change, so it is a timedomain AC technique. 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 ohmic resistance may be determined. This method works quite well, and has been used for many years as a measurement technique. Values may be verified with a digital oscilloscope and compare favorably with other data. 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 4.

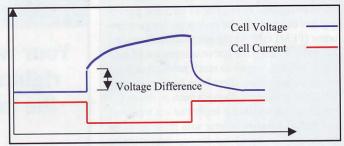


Figure 4. Typical Current Interrupt Waveform

ac Resistance Method - this method uses a 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. A distinct disadvantage of this method is that 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

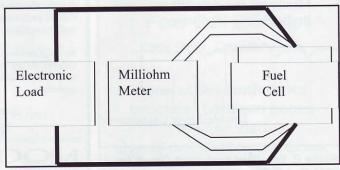


Figure 5. AC Resistance Measurement Technique

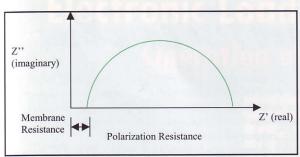


Figure 6. Nyquist Plot of Fuel Cell Impedance

difficulties stem from the millohmmeter not being intended to measure energy sources under load.

Electrochemical Impedance

Method - with this technique, a small amplitude AC current perturbation is introduced through the electronic load to impose a small sine wave 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 beginning at about 1 kHz to 10 kHz and decreasing to 1 Hz or lower frequency. This produces 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 not only used to determine the Ohmic resistance of the membrane, but also has the added benefit of providing 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 data, although previously discussed metrics such as membrane and polarization resistance are easily discerned from the Nyquist plot shown in Figure 6. Another disadvantage is the additional complexity and cost of the required equipment.

Each of these methods may be used to determine Ohmic resistance of the fuel cell membrane, and in the impedance case, valuable information about other cell parameters. Caution should be exercised when using any of these methods to verify the accuracy of the measurement by comparison with polarization curves and data obtained by other techniques.

Summary

A better understanding of electrical losses requires the following:

- · Overview of the AC measurement techniques available
- · Differences in the techniques
- · How they are applied
- · Interpreting measured data

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