

Unraveling Fuel Cell Electrical Measurements

James Niemann, Keithley Instruments, Inc.

ANYONE involved in the design, manufacture, application or repair of fuel cells, or fuel cell powered devices, needs cell data that is available only through direct electrical measurements. When properly interpreted, this data not only provides an understanding of how and why fuel cells work, but also indicates the health of operational cells, helps predict their life, reveals failure mechanisms, and provides insight into their suitability for specific applications.

Basic Operation of a Fuel Cell

A review of the reactions in a typical fuel cell provides a foundation for collecting useful electrical data. Many cells are designed around the type of reduction/oxidation (REDOX) reactions found in the hydrogen fuel cell. This cell architecture assumes H₂ and O₂ as reactants, an acidic electrolyte—which is typically a solid ion-conducting polymer—and two electrodes. The solid polymer membrane is sandwiched between the con-

ducting, catalyzed anode and cathode electrodes. See *Figure 1*.

The desired reactions in a hydrogen fuel cell are described by the equations in *Figure 1*. Usually these reactions yield only heat, but in a fuel cell the principal result is electrical energy. The electrons from the anode reaction flow through the external circuit and back to the surface of the cathode, supply-

ing the final cathode reactant. Measurements of these electrical and ionic currents are extremely useful in understanding a fuel cell's characteristics and operation.

Cell Energy and Voltage

A key variable in describing cell characteristics is a quantity called the *Gibbs free energy*. This describes the amount of free energy or chemical energy that a material possesses. Cell voltage and other electrical characteristics are related to the Gibbs free energy, which is a function of the electronic structure of the molecules undergoing reaction. In the case of a hydrogen fuel cell, the total energy available from its chemical reactions is equal to the free energy of the H₂ and O₂ reactants, minus the free energy of the reaction product, H₂O.

The potential difference (voltage) developed from the cell's electrical energy can be found from the following:

$$\text{Electrical power, } P = E * I \quad (\text{Eq. 1})$$

where *I* is the current, moving through a potential difference *E*, and *P* is the power delivered. Power is energy per unit time, and current is charge per unit time, thus:

$$W/t = E * Q/t \quad (\text{Eq. 2})$$

where *W* is energy in Joules, *t* is time in seconds, and *Q* is charge in Coulombs.

By eliminating the time variable,

$$W = E * Q \quad (\text{Eqn. 3})$$

W represents the energy required to move a charge *Q* through a potential *E*.

The Gibbs free energy can be equated to *W* and the equivalent heat energy released when hydrogen and oxygen react (undergo

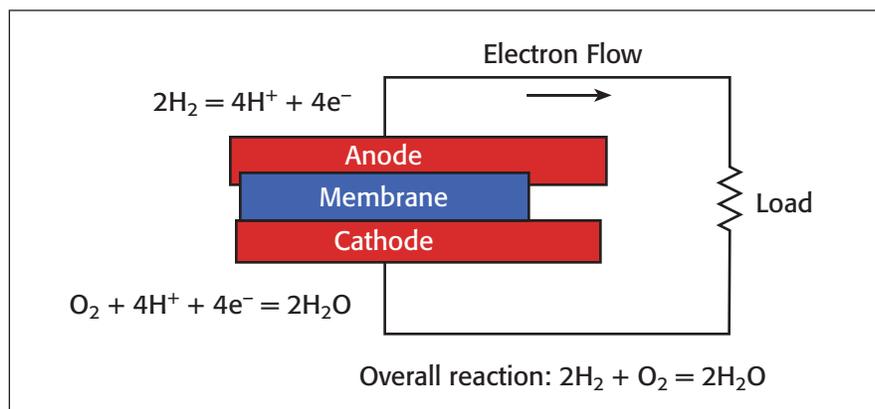


Figure 1. General construction and reactions in a hydrogen fuel cell with an acid electrolyte.

combustion). To do this, consider a quantity of reactant equal to one mole, or Avogadro's number ($6.02 \cdot 10^{23}$) of molecules. The quantity Δg_f can be substituted for W in *Equation 3* if the quantity of charge oxidized at the anode and subsequently reduced at the cathode for one mole of reactant are matched.

To quantify the charge, Q , recognize that in a fuel cell two electrons per molecule of H_2 are released when H_2 disassociates at the anode. So on a molar basis, 2 ($6.02 \cdot 10^{23}$) electrons are oxidized at the anode. By using the Faraday constant, F , [$F = (\text{Avogadro's number}) \cdot (e) = 96485 \text{ Coulombs}$], which is the charge on one mole of electrons, the electrochemically generated voltage can then be expressed as:

$$E = \frac{\Delta g_f}{F} \quad (\text{Eq. 4})$$

To find the actual voltage, Δg_f must be found from published tables or from an experiment done under specific environmental conditions. For a PEM (proton exchange membrane) cell design, the voltage can take on values between 1.1 and 1.23V, depending on temperature and pressure.

Equation 4 expresses theoretical cell voltage under specific operating conditions. In practice the voltage between cell terminals (and resulting energy generation) is always less than this value. The amount of this difference can be used as an indicator for the health and performance of the cell.

Polarization Curve

The most common electrical test of a cell is a set of measurements that create the polarization curve (*Figure 2*), which is simply the steady-state current vs. voltage curve of the cell. The three regions of operation labeled in *Figure 2* are due to internal cell losses.

In the activation region, the cell voltage drops quickly under even a small load current. This decrease begins when the load current exceeds the normal forward/reverse reaction rate (exchange current) at the cathode. (Note: the anode reaction has a higher rate than the cathode reaction.) Parasitic corrosion reactions within the cell may alter the current where the cell voltage first begins to drop.

After the initial drop, the cell voltage continues to decrease due to resistive losses in the ohmic region. In response to increasing load current in this region, the forward reaction at each electrode increases relative to the reverse reaction. It is the energy required to accomplish this change that is indirectly responsible for the decrease in cell voltage.

At some point, an increasing load becomes excessive, demanding more fuel than the anode and cathode flow fields can support. This is generally called mass transport loss, and that region of the polarization curve is labeled as such.

Although not evident on the polarization curve, all three losses (activation, ohmic,

and mass transport) are present throughout its entire length. The ohmic losses appear small at low currents when compared to the activation losses in the first part of the curve. Likewise, the activation losses appear small when compared to the ohmic losses when the cell currents are larger (in the ohmic region).

As cell voltage is reduced due to these losses, the electrical efficiency of the cell is also reduced. A very rough approximation is that cell efficiency is equal to cell voltage expressed as a percentage, i.e., a cell voltage of 0.7V represents a cell operating at about 70% efficiency.

Over-Potential and Related Issues

Over-potential is a phenomenon related to cell voltage and is far more important than efficiency, because it relates to the reliability and lifetime of a cell. To better understand this phenomenon and properly test for it, consider the simple electrical model of a cell in *Figure 3*. This figure models the internal losses that influence the shape of the polarization curve shown in *Figure 2*.

In a real cell, the ohmic loss due to internal resistance is responsible for internal heating and real power loss. However, the activation voltage loss has the greatest influence on over-potential. The energy required to drive the anode and cathode reactions in the forward direction give rise to this loss in cell voltage. All chemical reactions, even the exothermic variety, require some small activation energy. More reactions per unit time (a higher load current impressed upon the cell) require increasing amounts of activation energy due to the larger number of reactions. The result is a greater activation voltage drop, called over-potential.

In the model of *Figure 3*, the apparent energy dissipated in charge transfer resistances as load current flows through them actually represents the activation energy of the anode and cathode reactions. Since these reactions are slow, charge will develop at the electrode surfaces with the electrolyte (membrane) forming a capacitance component called the double layer capacitor. Double layer capacitance and charge transfer resistance change dramatically with load. This is why measurements of these elements must be undertaken over the entire polarization curve.

Activation energies for different types of

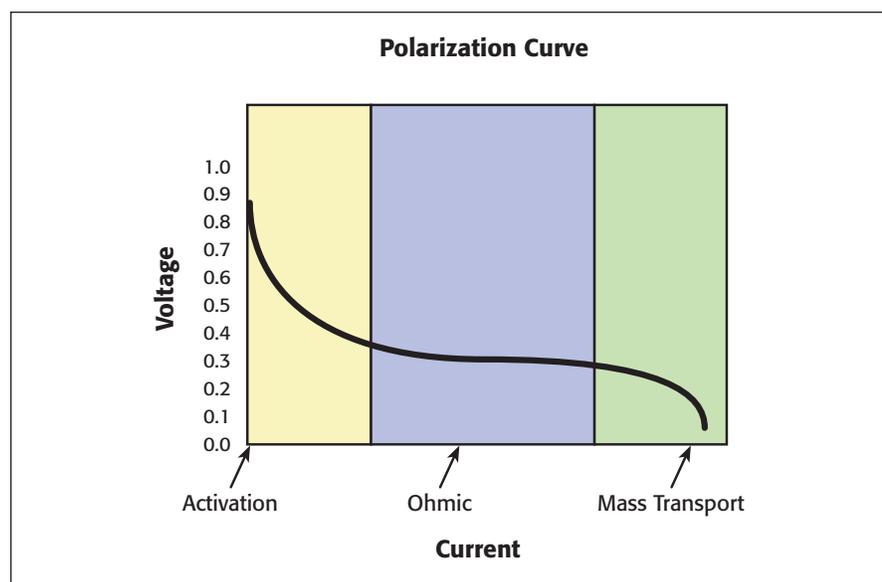


Figure 2. A plot of steady-state current vs. voltage measurements taken on a fuel cell generates an electrochemical polarization curve. The general shape of the curve is due to internal cell losses.

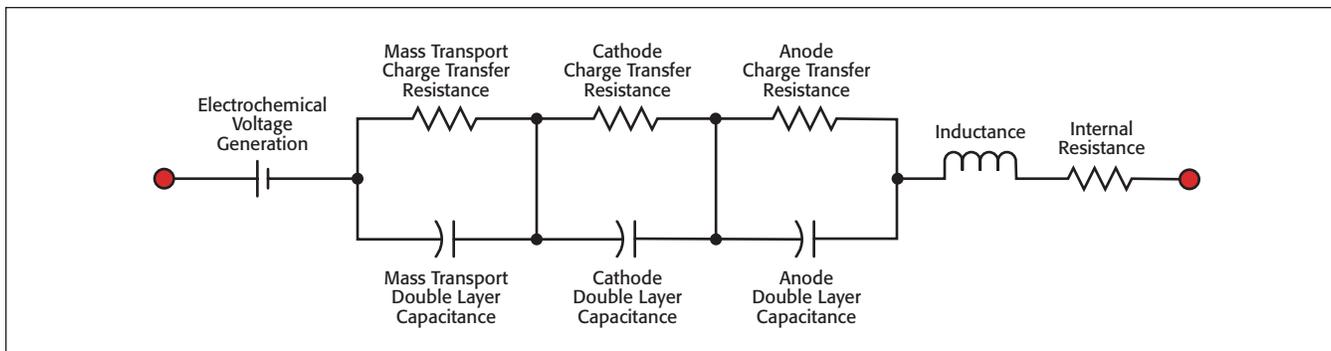


Figure 3. An “all-frequencies” electrical model of a fuel cell during normal operation.

electrochemical reactions originate within the cell itself. It follows that the value of the cell voltage can influence the rate of different reactions at the cell anode and cathode surfaces. For example, low cell voltages can favor parasitic corrosion reactions.

Life and reliability problems are accentuated when the cell operates in the mass transport region, where the electrode flow fields fail to keep up with reactant delivery appropriate for the load. In this case, since only ions are capable of traveling through the membrane, a spurious REDOX reaction is responsible for the remaining load current that is unable to be provided by the intended electrode (cathode) reaction. Here the cell voltage can drop precipitously (below 0.5V in *Figure 2*). If load current is maintained at such an elevated level, reduction of the fuel cell electrode surfaces is possible.

The general shape of the polarization curve provides insight into the proper measurement techniques for testing a specific fuel cell. By way of comparison, in electrochemistry studies it is common practice to fix a cell’s potential (potentiostatic control) and measure the resulting cell current. However, the best technique for fuel cell measurements is to force a cell current (galvanostatic control) and measure the resulting voltage.

The reason for this is that a good cell with low membrane ionic resistance will have a flattened ohmic region. (See *Figure 2*). If potentiostatic control is used, even small variations in the voltage can cause large changes in load current. In addition, potential is very difficult to control in the presence of a load capacitance, especially when its magnitude approaches that of the double layer capacitance of even a moderately sized cell. For this reason, galvanostatic control should be used in fuel cell polarization testing. Fur-

thermore, since cell membrane resistances are very low, accurate measurements of cell parameters can only be made if the load presented to the cell is free of noise. Low noise source-measure units are available that allow either galvanostatic or potentiostatic control, making measurements over the entire length of a polarization curve much easier and more accurate.

Internal Resistance Measurements

There are many electrical effects that occur during a fuel cell reaction that makes measurements of these complex devices difficult. The real component of the cell impedance, referred to as the internal resistance or membrane resistance, is critical to the health and performance of the cell. It is responsible for the real component of the energy lost by operating the cell under load. For this reason, determining the value of this ionic resistance is very important.

Internal ionic resistance measurements can be used to monitor the membrane humidification since the two values are functionally related. Humidification is required to maintain a low ionic resistance throughout the membrane, which of course reduces resistive losses. The membrane humidity will naturally increase as water is produced at the cathode for an increasing load current, or will decrease as the load current is reduced (accompanied by less water production). Temperature should also be considered in these measurements since membrane operation is correlated with that variable.

Internal resistance is usually determined by measuring the cell voltage at a specific load current, then briefly interrupting the load current and measuring cell voltage during the interruption. Though simply described, this is not a trivial task, due mostly

to the interaction of the cell inductance with the double layer capacitance, and the performance of the current source. When selecting a current source for these measurements, a major consideration is the performance of the source as it establishes the interrupt in the presence of load impedance and the cell current, which can be large.

When determining internal resistance via the interrupt method, what is actually measured is the magnitude of cell impedance, including cell inductance and double layer capacitance. The magnitude of the impedance will change with frequency due to the reactive components of the cell. Due to the small value of a cell’s real resistance, the frequency of the measurement must be high enough (i.e., current interruption short enough) to eliminate the effects of the total cell reactance. When the instrumentation is set properly, the impedance associated with cell inductance exactly cancels the impedance of the double layer capacitance, leaving only the internal resistance in the measurement results.

In order to measure the high frequency resistance of the model shown in *Figure 3*, the interruption must be brief enough that the double layer capacitances and electrode resistances maintain their small signal values as modeled. These values are only valid at a specific cell polarization or loading. The anode and cathode model values represent the anode and cathode chemistry charge transfer resistances and double layer capacitances. These quantities effectively model the anode and cathode reaction rates.

In the measurements for this model, it is helpful to partially interrupt the load current for a short period of time, rather than using a full interrupt equal to the magnitude of the load current. If the cell disturbance is

only a small percentage of the polarization current, then the cell chemistry and resulting small signal model remain unaffected by the disturbance. This partial interrupt may allow a longer interrupt time as required to eliminate the reactive components of the measurement. An appropriate interrupt time depends on the size and type of cell, but is typically between 20 and 200 microseconds. Instrumentation useful in the interrupt measurement are shown in the references.

Nyquist Plot

A Nyquist or Cole-Cole plot (*Figure 4*) describes more about the internal operation of a cell than any other electrical test and analysis technique. It combines all lumped elements of the model (*Figure 3*) into a single complex number consisting of a magnitude and phase angle, or equivalently, as real and imaginary components of impedance at each frequency. The real part of the impedance is plotted on the x-axis, and the imaginary component on the y-axis. The portion of a Nyquist plot that crosses the x-axis represents the real resistance as measured by the interrupt measurement described above.

Nyquist analysis provides useful information on the reactions that are occurring in a fuel cell. As shown earlier, the chemical reactions at the anode and cathode are of the REDOX variety. As such, elec-

trons are liberated at the anode (the oxidation process) and are subsequently mopped up at the cathode (the reduction process). In a hydrogen fuel cell, exactly two electrons are processed per individual reaction. Electrical testing of the cell current essentially measures the reaction rates by counting these electrons as they move through the external circuit, exactly two for every reaction.

In a Nyquist analysis, useful electrochemical information is usually found in the 50kHz to 0.01Hz (or even lower) range. (See *Figure 4*.) In the resulting model, a slow reaction is represented by a large RC time constant of the charge transfer resistance and the electrode capacitance, or physically as a delay in voltage changing on the double layer capacitance of the cell when a step load current is applied.

Thus, a Nyquist representation of measurement data can separate the charge transfer resistances and their reaction time constants for all intended REDOX reactions taking place in the cell. Additionally, any other activity, such as parasitic corrosion reactions, membrane resistance, double layer capacitance, and cell inductance are also isolated. Each reaction is separated in the Nyquist plot as a separate “bump” or semicircle. Although the impedance instrumentation measures a lumped value of all model elements at any frequency, when the data is plotted in

Nyquist form the individual reaction information is regained.

Making Measurements Under Galvanostatic Control

As alluded to earlier, there are good reasons for using current control in polarization curve measurements. These include the following:

1. Current control allows the superposition of multiple source and measurement instruments on a single cell or stack of cells.
2. Fuel cells are low impedance devices and can be measured with lower noise by sourcing current and measuring voltage rather than vice versa.
3. Current sources are more stable than voltage sources with the highly capacitive load of a fuel cell, resulting in precise interrupts (accurate internal resistance measurements) and high frequency AC impedance information.

Low internal resistance argues against potentiostatic control in fuel cell testing. Fuel cells (especially large ones) have internal resistance in the mΩ to μΩ range when measured at high frequency (short interrupt). Since potentiostatic control fixes the cell potential with respect to the voltage measure terminals, noise in the potential driving the cell will generate significant noise current

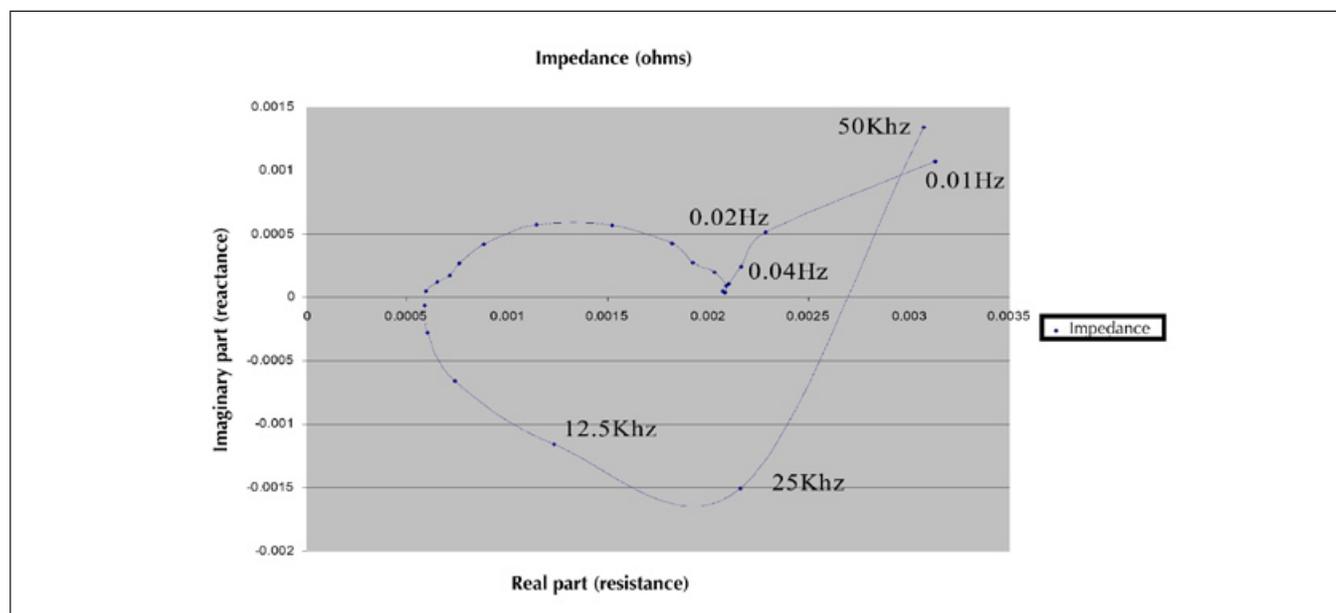


Figure 4. Example of a Nyquist impedance plot of measurement data collected on a single cell under galvanostatic control using the current interrupt technique. This utilizes individual cell voltage measurements, as well as measurements of the source current and polarization current, and can be applied to a single cell buried in a stack. (Data collected on a cell supplied by the Fuel Cell Control Lab, University of Michigan.)

through the cell's low impedance. For example, the internal resistance of a large cell under a 55A load can be as low as $560\mu\Omega$. A 1% stimulus yields a 0.55A test current, and 0.55A through $560\mu\Omega$ generates a 308 μ V signal. This needs to be measured to a few decimal places (i.e., about 100nV resolution) to accurately calculate internal resistance. At this level, voltage noise under potentiostatic control causes large noise errors in the measurements.

By contrast, under galvanostatic control, a relatively large current is forced through the cell, which is measured as a voltage across an instrument's internal current sensing resistor. Since this resistance is decades larger in value than a cell's internal resistance, noise in the measurement is a much smaller percentage of the signal. Similarly, a relatively large voltage signal can be accurately measured across the cell terminals.

Galvanostatic control allows the separation of the polarization current and the test current by taking advantage of high current source output impedance and applying superposition. *Figure 5* illustrates current source Norton models (voltage source in series with a high internal resistance) and two possible test configurations for current mode-testing. Since the test signal is applied by a current source with high output impedance over a wide range of frequencies, all of the polarization current will flow through the load, not through the impedance test current source.

In this test methodology the cell voltage, test current, and polarization current must all be measured in order to compute the cell impedance over frequency. (Voltage sense leads should be placed directly on the equipotential surfaces of the cell's anode and cathode to assure accurate measurements.) Polarization current measurements are important because they reflect polarization noise, and that small portion of the test current that runs through the polarization current source rather than the cell.

Conclusions

Polarization curves, internal resistance, and impedance plots provide essential information that largely determines the suitability of a particular cell for an end product application. However, the test instrument and current signal must not generate unwanted noise

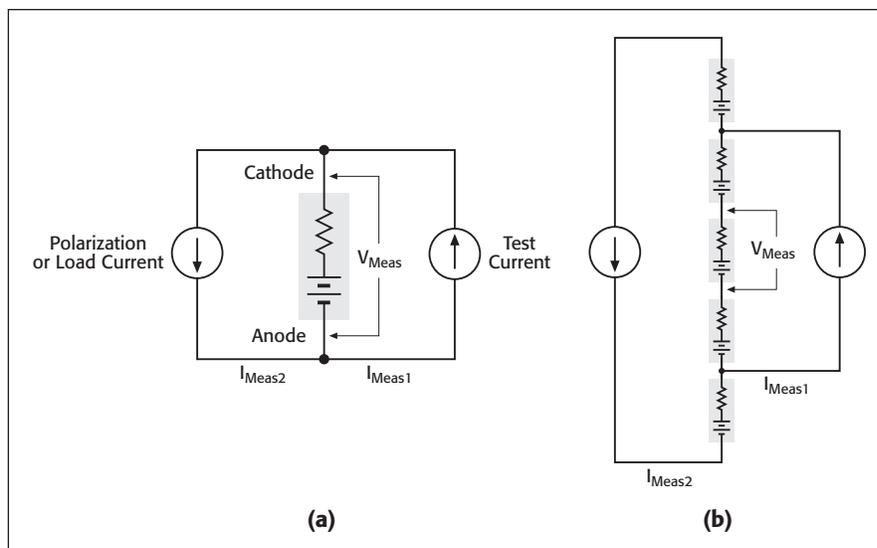


Figure 5. Norton models of fuel cell test circuits with loads applied under galvanostatic control: (a) an individual cell; (b) a single cell buried in a stack.

AC+DC Current Source and Nanovoltmeter Simplify Low Power/Low Voltage Measurements in Demanding Applications

Determining the internal impedance of a fuel cell using the current interrupt method requires precise coordination of the current source and voltage measuring instrument. To facilitate this demanding task, Keithley developed its Model 6221 AC+DC current source and Model 2182A Nanovoltmeter. These two instruments have features that make it easy to create a tightly integrated fuel cell test system that provides highly accurate measurements of the test current, cell voltage, and internal resistance.

The Model 6221 is the only commercially available current source waveform generator for creating and outputting complex waveforms. It allows pulsed I-V measurements and is a replacement for AC resistance bridges and lock-in amplifiers (when used with Model 2182A). This combination can be treated as a single instrument, making it easy to perform a partial interrupt (between 50 and 200 μ s) of the load current, rather than using a full interrupt equal to the magnitude of the load current. This means that the cell chemistry and resulting small signal model remain unaffected by the disturbance, facilitating the measurements to accurately determine internal cell resistance as low as 10n Ω .

Of course, the test instrument and current signal must not allow unwanted noise to enter the measurements. Incorporated into the Model 6221 and Model 2182A is a delta measurement mode, that can cancel thermoelectric offsets that cause measurement drift over time. Moreover, this technique produces results in half the time of previous techniques, and allows the source to control and configure the nanovoltmeter; so setting up the measurement takes just two key entries on the front panel. The improved cancellation and higher reading rate reduces measurement noise to as little as 1nV. Free control software provided with the Model 6221 includes a tutorial that “walks” users through the delta mode set-up process.

In pulsed and interrupt testing, the Model 6221 provides microsecond rise and fall times on all ranges, with pulse widths as short as 50 μ s. The Model 6221/2182A combination synchronizes the pulse and measurement—a measurement can begin as soon as 16 μ s after the Model 6221 applies the pulse. The entire pulse, including a complete nanovolt measurement, can be as short as 50 μ s. Line synchronization between the Model 6221 and Model 2182A eliminates power line related noise. The Model 6221 can also generate standard and arbitrary waveforms at frequencies ranging from 1mHz to 100kHz, at an output update rate of 10 megasamples/second, with current magnitudes that range from 1pA to 100mA. A built-in Ethernet interface provides easy remote control without a GPIB controller card.

and ringing into the load, or errors will creep into the internal resistance measurements.

While the polarization curve yields data related to basic cell performance, more detailed information can be found by measuring internal resistance and impedance, and analyzing this data with a Nyquist plot. The membrane humidity, as indicated by a cell's internal resistance, is particularly useful in evaluating whether the cell is in an appropriate state to deliver a rated load. Impedance plots are used to evaluate the reaction rates at the anode and cathode, and identify any parasitic reactions. The performance of the anode and cathode flow fields are also apparent in a Nyquist plot. 

References

1. *Fuel Cell Systems Explained*, Wiley, 2000, James Larminie, Andrew Dicks.
2. *Electrochemical Methods: Fundamentals and Applications*, Wiley, 2001, Allen J. Bard, Larry R. Faulkner.
3. *Achieving Accurate and Reliable Resistance Measurements in Low Power and Low Voltage Applications*, Keithley Instruments white paper, 2004.

About the Author

James Niemann is a Staff Engineer with Keithley Instruments in Cleveland, Ohio, where he is responsible for designing instrumentation used in low-level measurements. He earned a Bachelor of Science degree in Electrical Engineering from the University of Akron. He has been awarded three patents for his work and has 15 years of experience in instrumentation design.

Specifications are subject to change without notice.

All Keithley trademarks and trade names are the property of Keithley Instruments, Inc.
All other trademarks and trade names are the property of their respective companies.

KEITHLEY

Keithley Instruments, Inc.

28775 Aurora Road • Cleveland, Ohio 44139 • 440-248-0400 • Fax: 440-248-6168
1-888-KEITHLEY (534-8453) • www.keithley.com

© Copyright 2004 Keithley Instruments, Inc.
Printed in the U.S.A.

No. 2581
1204