Electrochemical Impedance Spectroscopy (EIS): A Powerful and Cost-Effective Tool for Fuel Cell Diagnostics

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool that you can use to characterize limitations and improve the performance of fuel cells. There are three fundamental sources of voltage loss in fuel cells: charge transfer activation or "kinetic" losses, ion and electron transport or "ohmic" losses, and concentration or "mass transfer" losses. Among other factors, EIS is an experimental technique that can be used to separate and quantify these sources of polarization. By applying physically-sound equivalent circuit models wherein physiochemical processes occurring within the fuel cell are represented by a network of resistors, capacitors and inductors, you can extract meaningful qualitative and quantitative information regarding the sources of impedance within the fuel cell. EIS is useful for research and development of new materials and electrode structures, as well as for product verification and quality assurance in manufacturing operations.

This article provides a quick primer on EIS with an introduction to its application in fuel cell testing and research.

Instrumentation and measurement basics

During an impedance measurement, a frequency response analyzer (FRA) is used to impose a small amplitude AC signal to the fuel cell via the load (***Figure 1***). The AC voltage and current response of the fuel cell is analyzed by the FRA to determine the resistive, capacitive and inductive behavior - the impedance - of the cell at that particular frequency. Physicochemical processes occurring within the cell – electron & ion transport, gas & solid phase reactant transport, heterogeneous reactions, *etc.* – have different characteristic time-constants and therefore are exhibited at different AC frequencies. When conducted over a broad range of frequencies, impedance spectroscopy can be used to identify and quantify the impedance associated with these various processes.

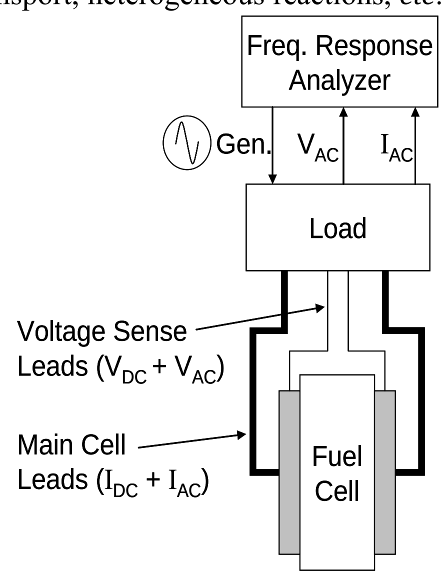


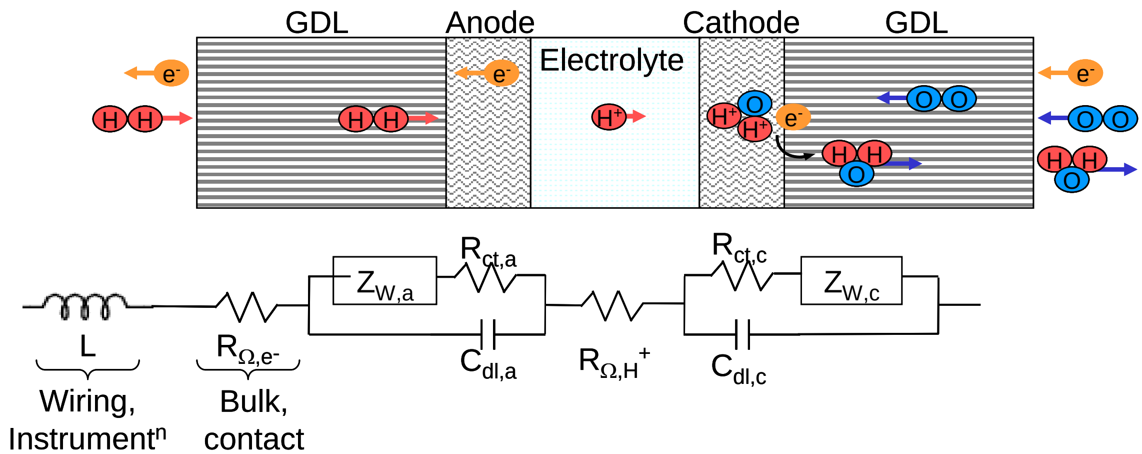
Figure 1. Instrumentation for EIS of fuel cells.

Advantages of EIS:

- Measurements can be made under real-world fuel cell operating conditions, *e.g.*, open circuit voltage or under load (DC voltage or current).
- Multiple parameters can be determined from a single experiment.
- Relatively simple electrical measurement that can be automated.
- Can verify reaction models, and characterize bulk and interfacial properties of the system, *e.g.*, membrane resistance and electrocatalysts.
- Measurement is non-intrusive – does not substantially remove or disturb the system from its operating condition.
- A high precision measurement – the data signal can be averaged over time to improve the signal-to-noise ratio.

Equivalent Circuit Modeling

Equivalent circuit modeling of EIS data is used to extract physically meaningful properties of the electrochemical system by modeling the impedance data in terms of an electrical circuit composed of ideal resistors (R), capacitors (C), and inductors (L). Because we are dealing with real systems that do not necessarily behave ideally with processes that occur distributed in time and space, we often use specialized circuit elements. These include the generalized constant phase element (CPE) and Warburg element (Z_W). The Warburg element is used to represent the diffusion or mass transport impedances of the cell. An example of a generalized equivalent circuit element for a single cell fuel cell is shown below.



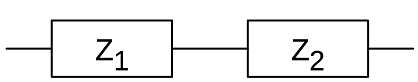
Key: GDL = gas diffusion layer, dl = double layer, ct = charge transfer, a = anode, c = cathode.

In the equivalent circuit analog, resistors represent conductive pathways for ion and electron transfer. As such, they represent the bulk resistance of a material to charge transport such as the resistance of the electrolyte to ion transport or the resistance of a conductor to electron transport. Resistors are also used to represent the resistance to the charge-transfer process at the electrode surface. Capacitors and inductors are associated with space-charge polarization regions, such as the electrochemical double layer, and adsorption/desorption processes at an electrode, respectively.

The defining relation and impedance for ideal bulk electrical elements are shown below.

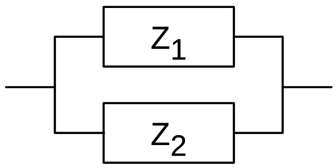
		Defining Relation	Impedance
Resistor		$V = I \times R$	$Z_R = R$
Capacitor		$I = C\dfrac{dV}{dt}$	$Z_C = \dfrac{1}{j\omega C} = -\dfrac{j}{\omega C}$
Inductor		$V = L\dfrac{dI}{dt}$	$Z_L = j\omega L$

The impedance of elements in series is additive,



$$Z_{Total} = Z_1 + Z_2 \ .$$

The impedance of elements in parallel is the inverse of the sum of the inverse of impedances,



$$\frac{1}{Z_{Total}} = \frac{1}{Z_1} + \frac{1}{Z_2} \ .$$

Representation of Impedance Data

EIS data for electrochemical cells such as fuel cells are most often represented in Nyquist and Bode plots as shown in ***Figure 2***. Bode plots refer to representation of the impedance magnitude (or the real or imaginary components of the impedance) and phase angle as a function of frequency. Because both the impedance and the frequency often span orders of magnitude, they are frequently plotted on a logarithmic scale. Bode plots explicitly show the frequency-dependence of the impedance of the device under test.

A complex plane or Nyquist plot depicts the imaginary impedance, which is indicative of the capacitive and inductive character of the cell, versus the real impedance of the cell. Nyquist plots have the advantage that activation-controlled processes with distinct time-constants show up as unique impedance arcs and the shape of the curve provides insight into possible mechanism or governing phenomena. However, this format of representing impedance data has the disadvantage that the frequency-dependence is implicit; therefore, the AC frequency of selected data points should be indicated. Because both data formats have their advantages, it is usually best to present both Bode and Nyquist plots.

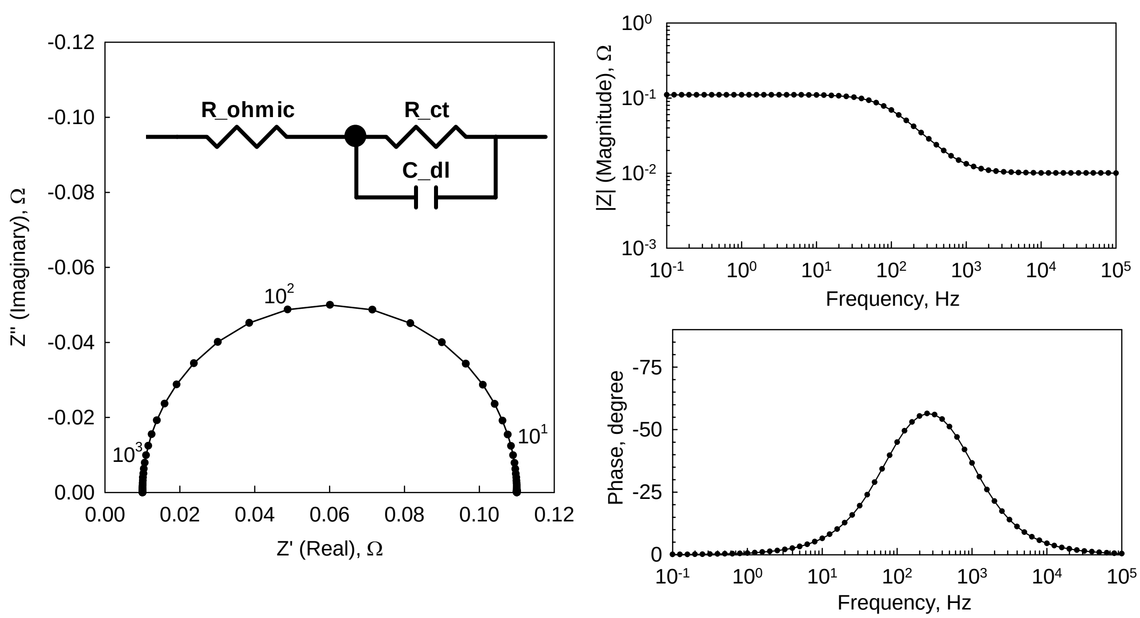
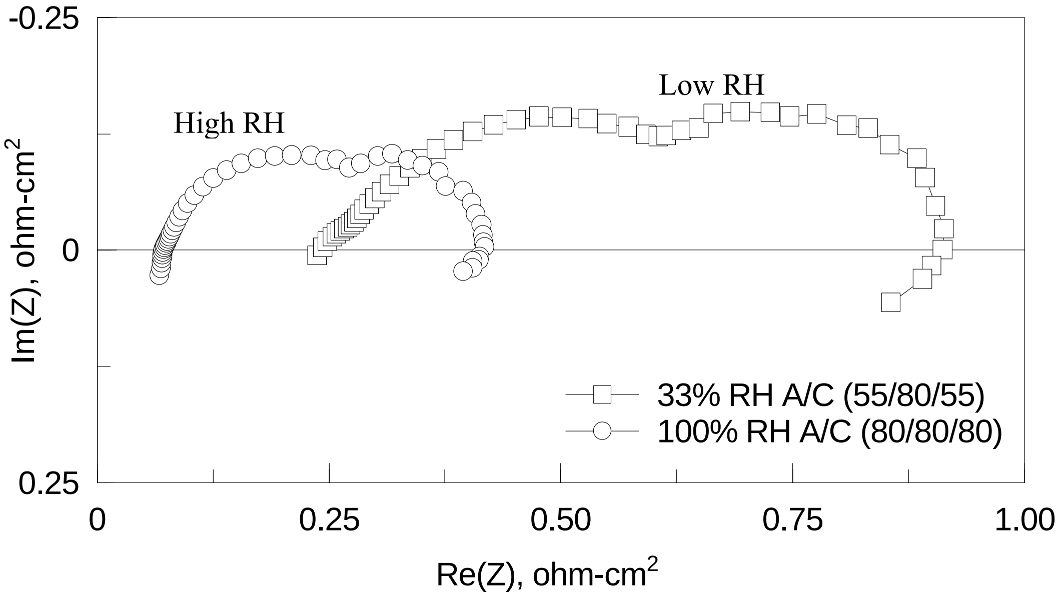


Figure 2. Impedance plots for the indicated simple RC circuit where R_{ohmic} = 0.01 Ω, R_{ct} = 0.1 Ω and C_{dl} = 0.02 F. For clarification, 3 frequencies (10^3, 10^2 and 10^1 Hz) are labeled in the complex plane (Nyquist) plot.

Case Study: Impact of Humidity on Fuel Cell Performance

Humidity plays a very important role in determining the performance of polymer electrolyte membrane (PEM) fuel cells. As revealed in the EIS data shown in the Nyquist plot below, low humidity impacts the fuel cell in three ways: (*i*) the increase in the high frequency resistance of the cell, which is dominated by the membrane resistance, indicates that the conductivity of bulk electrolyte (membrane) decreased at lower humidity, (*ii*) the 45° angle at high frequency is characteristic of a distributed ohmic resistance in parallel with a distributed double layer and is indicative of non-negligible ohmic (electrolyte) resistance within the catalyst layer, and (*iii*) an increase in the charge transfer resistance for the oxygen reduction reaction is shown as nn increase in the size (diameter) of the high frequency impedance arc.



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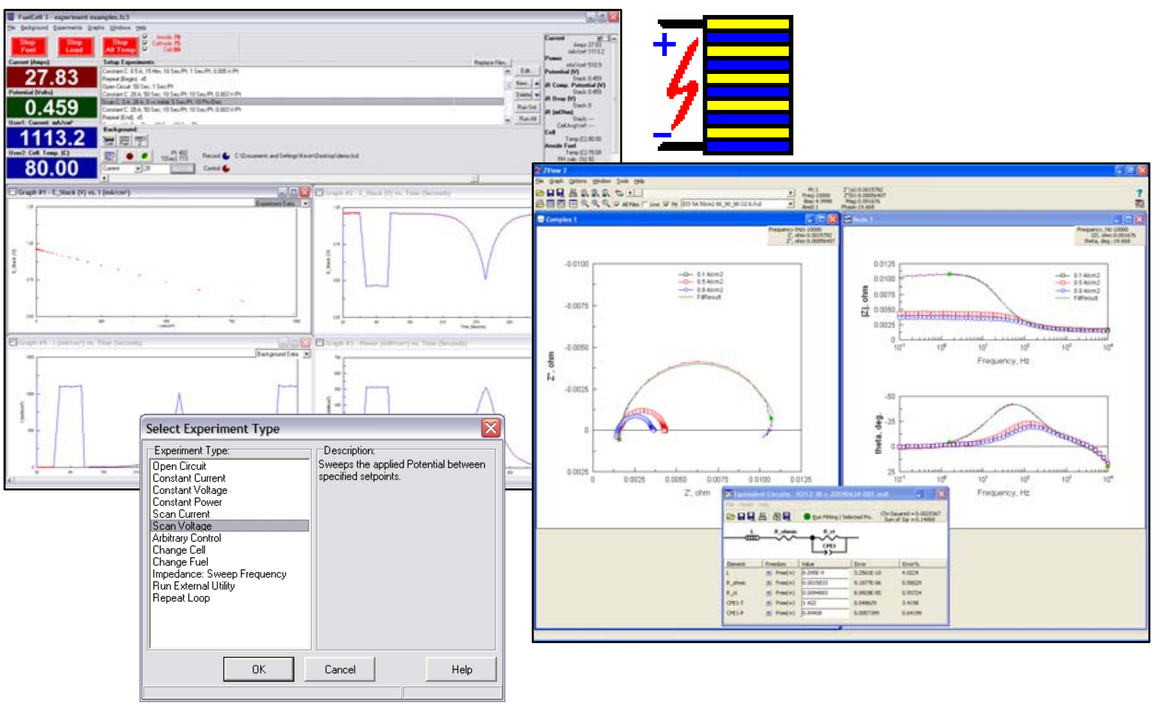
Scribner Equipment for Fuel Cell EIS & HFR Measurements

Scribner offers an integrated FRA for seamless EIS and HFR measurements with the 850e Fuel Cell Test System and 890 Fuel Cell Test Loads ***for under $5,000***. Compare this to a typical stand-alone EIS system which can cost as much as $25,000!

Scribner's integrated FRA is specifically designed for fuel cell testing and is optimized to work with our custom-designed electronic loads and integrated test systems.

FuelCell® software has built-in features for whole-cell and half-cell EIS and HFR. EIS data acquired with FuelCell® are fully-compatible with ZPlot® / ZView™, internationally-recognized software for EIS data processing, equivalent circuit analysis and graphing.



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