TechnicalNOTE

GAMRY INSTRUMENTS

Accuracy Contour Plots

Introduction

Electrochemical Impedance Spectroscopy (EIS) is a valuable, versatile analytical tool for resolving electrochemical processes. The fundamentals of this frequency-based AC technique are described in detail elsewhere (http://www.gamry.com/App_Notes/EIS_Primer/EIS_Primer.htm). This document describes the effect of the potentiostat on the accuracy of an impedance measurement.

The impedance measurement is a collective representation of all the components of the system -- the cell, the instrument, and the connecting cables. It is important to consider the limits of your instrument, particularly at extreme frequencies or impedances. *Not all measurements you can make can be trusted.*

Gamry Instruments' Reference 600 Potentiostat serves as a case study for this discussion, but the principles detailed in this document are general to all computer-controlled potentiostats. The goal of this document is to provide the necessary tools to determine the limits of the instrumentation. Here, the response of an idealized cell (resistors or capacitors) is evaluated and mapped as an Accuracy Contour Plot. An electrochemical cell with an impedance within this plot can be accurately measured, contingent on the assumptions of EIS theory – a linear, stationary system, without current drifts, and adequate cell design.

The Accuracy Contour Plot shows the accuracy of a given measurement system in an ideal world with appropriately realistic parameters. This Application Note focuses on the Accuracy Contour Plot, compares it to the Open Lead Curve, and gives experimental design advice to researchers using impedance to study different applications.

The Accuracy Contour Plot

Figure 1 is a general example of an Accuracy Contour Plot. This map is a log-log plot (fashioned as a Bode-type plot). Potentiostats are multiuse instruments; scientists in different applications are concerned with the system performance in regions near different limits. A description of each labeled limit in the Accuracy Contour Plot follows.

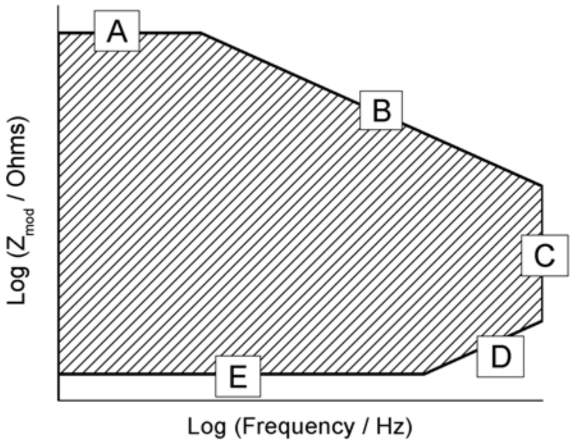

Figure 1. Generic form of an Accuracy Contour Plot.

Limit A (Maximum Measurable Impedance)

This portion of the map represents the upper limit of the impedance that can be accurately measured by the instrument. Researchers in the fields of **coatings** and **membrane** research often work in this impedance realm. The manufacturer of the potentiostat may state this value in their Hardware Specifications. It is less than, but related to, the Input Impedance of the potentiostat's electrometer.

The value of the magnitude of the impedance at this point is limited by drift in the current response, by drift in the instrument's current measurement circuitry, or internal resistance in the instrument. (Drift causes a random phase response; whereas, an internal resistance causes the phase to approach 0^o). Cell currents in the region near this limit are exceedingly low. For discussion, if we assume that the sample has an impedance of 10^{12} Ω...a 10 mV signal is only passing 10^{-14} Amps. This is only 10 fA !!

The impedance magnitude where the values become resistive (independent of frequency) is related to the amplitude of the excitation signal. The accuracy of the impedance measurement at this limit can be increased by increasing the amplitude of the excitation. At large excitations the accuracy is limited by the internal resistance of the instrument.

Limit B (Lowest Measurable Capacitance)
This portion of the map represents the accuracy limit for low capacitance capability of the instrument. The value of this capacitive limit is a concern to scientist evaluating semiconductors, dielectrics, or organic coatings (such as paints) on metal substrates with good barrier properties. *The thicker the coating, the lower its capacitance.*

On this plot, capacitors are represented by a line with slope equal to –1, determined by the relationship of capacitance, frequency, and impedance (see Equation 1). The smaller the value of capacitance, the larger the intercepts at the axes, shifting the line towards the upper right (further away from the origin). Larger capacitances shift the diagonal line towards the lower left.

$$C = \frac{-1}{(\omega Z_{\text{mod}})} \tag{1}$$

The position of Limit B is specified by giving the value of the capacitor whose impedance corresponds to this line.

This provides an easy to understand guide line for the trustworthiness of a measurement.

Limit C (Maximum Measurable Frequency)
This line represents the frequency of the AC signal that the potentiostat's manufacturer specifies as the maximum frequency for an EIS measurement. This limit is considered the instrument's "sweet spot". A sample within this range of impedance is measured with the highest degree of accuracy, also specified by the manufacturer. In other words, the Accuracy Contour Plot describes the range of impedances measurable at the maximum excitation frequency. Note that the entire range of impedance is not accessible over the entire range of frequency. However, a high proportion of electrochemical cells have impedance values within this range.

Several instrumental factors can affect measurements taken at Limit C, such as, Slew Rate (description of how fast an Op-Amp can respond to a change in input), frequency response of components and A to D jitter.

Though the plot shows a high degree of accuracy from the instrument, the cell itself may have limitations to cause experimental artifacts. One example of such an artifact is due to the slow response of the Reference Electrode (remember, you are asking the cell to respond to a million sine waves of signal in the span of 1 second). We will have upcoming Technical Note on advice for a "high-speed" (pseudo) Reference Electrode.

Limit D (Low Impedance at High Frequencies)
The region near this limit is important for the high-frequency study of low-impedance samples. This area is common to **batteries** and **fuel cells**.

The Accuracy Contour Plot identifies the limits of the potentiostat. Inductive signatures may appear in an user's impedance spectrum in the region near this limit. Inductive signatures will have a +90° phase in a Bode plot and appear as a straight line extending below the x-axis in a traditional Nyquist plot. This signature, often assigned to some physical/chemical process, may also be an artifact of the instrumentation. The primary culprit of this stray impedance is the pickup from the mutual inductance of the cell leads. The position of Limit D is specified by giving the value of the inductor that has the same Bode plot as Limit D.

Inductance describes a magnetic flux due to current flowing through a wire. Inductive pickup or influence occurs when the wire is moved in the field or the field itself is moved (here it is a phenomenon from the AC nature of the measurement). This inductive pickup varies with the magnitude of the current and placement of the cell leads. There is an extended discussion below on experimental practices to minimize this effect.

<u>Limit E (Lowest Measurable Impedance)</u>

Analogous to the discussion of region near Limit A (where the limit is defined by the ability to measure small currents), at Limit E the potentiostat is limited by its ability to measure high currents. For example, applying a 10 mV signal to a system with an impedance of 0.01 Ω generates a current of 1 Amp!

If this exceeds the maximum current rating of the potentiostat, the impedance can not be measured, even with poor accuracy without decreasing the excitation level!

Example of an Accuracy Contour Plot

Figure 2 is an Accuracy Contour Plot for Gamry Instruments' Reference 600 Potentiostat. This plot describes the accuracy over which a range of impedances and frequencies can be measured under the specified conditions.

Note, this map is data measured with electrical components (resistors and capacitors). Figure 2 is not an estimate from the Open Lead Curve (See Below).

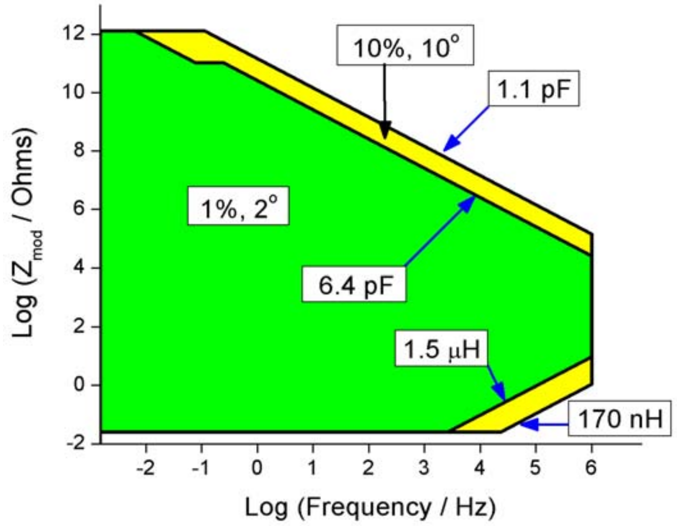

Figure 2. Accuracy Contour Plot for Gamry's Reference 600. The curve was generated by Potentiostatic EIS (10 mV rms, except Limit D which used 3 mV rms) on resistors and capacitors. The standard 60 cm cell cable was used.

Good Electrochemical Practices

Every electrochemical cell is unique. However, a general discussion follows (complete with advice) for scientists evaluating systems that fall into the previously mentioned regions near the different limits.

<u>High Impedance Systems (Limit A)</u>

Figure 2 shows that the Reference 600 can measure impedances on the order of 10^{12} Ω at a signal amplitude of 10 mV rms. One of the assumptions of EIS theory is that the system is linear. In general, this assumption is maintained by applying a small excitation amplitude (such as a default value of 10 mV). This small amplitude does not polarize the system and does not change its properties. In order to increase the confidence window of high impedance samples, you can increase the amplitude of the AC signal to 100 mV rms. With this larger signal, the instrument can accurately measure higher impedance systems, because similar currents are passed. Caution, large amplitude excitations may change the sample. Use with care.

EIS measurements at low frequency take a long time. Drift due to aging effects on the sample, temperature cycles, or mechanical disturbances are bound to limit the stability of the current. These drifts are seen in a Lissajou figure, an elliptically-shaped plot of current as a function of voltage. The Lissajou figure is Gamry's default active window in the EIS300 software.

High impedance samples, by definition, only pass small currents, which are easily swamped by noise; therefore, a Faraday Cage will improve the reliability of results from a high Z sample at typical AC amplitudes. A Faraday Cage is a grounded conductive shield that encases the electrochemical test cell. The Faraday Cage blocks electrostatic interferences from external sources from being picked-up in the leads. It does not have to be sophisticated (a coffee can will often suffice), but the continuity of the conductive path of the cage is crucial. This cage will isolate the cell from the environmental interferences such as the line frequency (50 or 60 Hz) or RF. A general guideline is that a Faraday Cage becomes important at currents below 100 nA.

Low Capacitance Samples (Limit B)

A capacitor is formed when two conductive plates are separated by a dielectric. Alligator clips, at the end of the cell cable, themselves act as the parallel plates of a capacitor, with the air between them as the dielectric. This capacitance is a function of the size of the clips (plates) and the distance that separates them. In air, this relationship (Equation 2) can be approximated by:

$$C = \varepsilon \frac{A}{d} \tag{2}$$

C represents the capacitance in Farads; ε is the permittivity of the dielectric medium (air is approximately that of vacuum; $8.85\text{x}10^{-12}$ F m^{-1}); *A* is the surface area of one clip (taken to be 2.5 cm^2); and *d* is the spacing between the clips. Using standard alligator clips separated by 2 cm, the capacitance will be on the order of 110 fF. Therefore, there is a 110 fF capacitive contribution in any measurement, just from axially placed alligator clips serving as the parallel plates of a capacitor. This capacitance is large enough to cause a finite phase shift.

To minimize this effect, design the cell with the alligator clips coming in radially (as opposed to axially). This minimizes the effective size of the "plate" thus reducing that stray capacitance. See Figure 3.

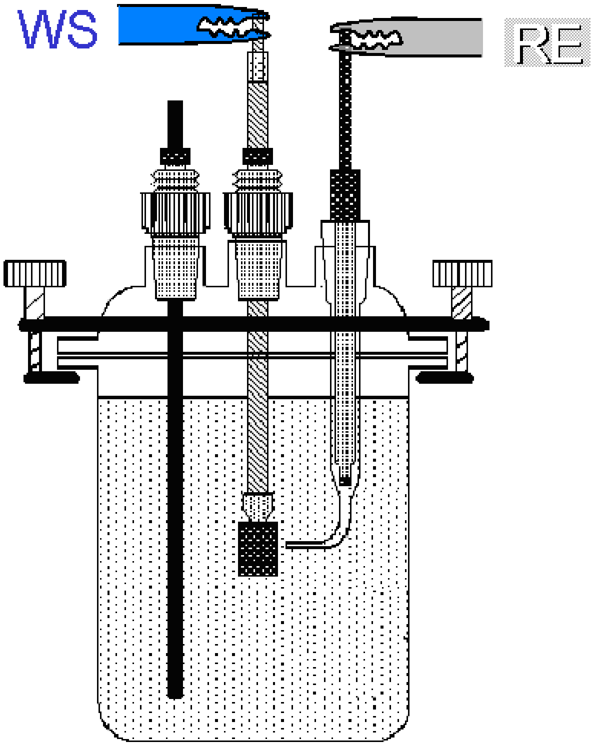

Figure 3. Preferred orientation for alligator clips to minimize the capacitive contribution from the clips (optimize plate area).

Also, Gamry's cell cables have driven shields to reduce capacitance of the lead.

Low Z Materials at High Freq. (Limits D and E)
Gamry uses a "Working Sense" (WS) lead to measure and control the potential difference versus the Reference Electrode (RE), and a separate "Working" (WE) lead to carry the current from the Counter Electrode (CE). If your potentiostat has only three cell leads, both responsibilities are assigned to one working electrode lead.

A *mutual inductive effect* determines Limit D. This limit is a function of the influence of a magnetic field generated by the current-carrying leads on the sense leads.

The practices described here are examples of experimental design by informed scientists permitting the instrument to function to its maximum capability. This information suggests that you should separate the cell-lead pairs as far as experimentally possible to minimize the inherent inductances of the leads and capacitance of the cell cable connections. Remember, trade-offs and limits exist in experimental design. While separating the leads minimizes the capacitance between the sense and current carrying leads, it will increase mutual inductance in the measurement.

Minimize the Field
Remember, current is carried between the Working (WE) and Counter Electrode (CE). This current passing through the wire creates a magnetic field. By physically twisting the WE and CE leads we minimize the radiated external field, because current is being carried in opposite directions. From your college physics course, the E ⊗ B cross-product relationship obeys the Right-Hand-Rule for each of the current-carrying leads. Since the current is flowing in opposite directions, your thumb points in opposite directions for each lead minimizing the external field.

Minimize the Pickup
By keeping the sense leads (RE and WS) close together, they "sense" the similar fields from the mutual (though minimized) inductance of the WE/CE pair described above. The electrometer of the potentiostat sees this as a common mode signal and compensates. Again, we physically twist the leads, because that ensures they remain in proximity. It is the pickup in the RE/WS pair of the inductive field generated by current flowing through the WE/CE pair that limits the performance of the system in the high-frequency low-impedance region.

Arrange the Pair
The properties that we witness are the fundamentals of a transformer. If your experiments are in the region where inductive pickup may limit performance (near Limit D), Loop Area between the sense WS/RE leads and between the current-carrying WE/CE leads needs to be minimized with a tightly-braided twist. This minimizes both broadcast and pickup of the magnetic field. Also, the distance between the pairs should be maximized. Arrange each pair so that they extend radially from the potentiostat and then approach the cell from opposite directions (180°), as shown in Figure 4.

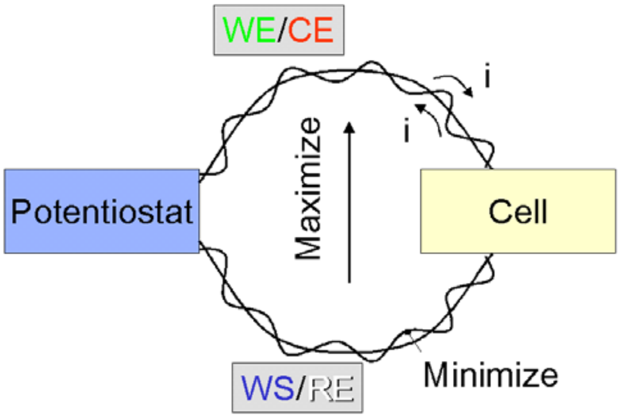

Figure 4. Diagram of recommended positioning to study a low-impedance sample, that is susceptible to inductive effects at high frequency.

The Open Lead Curve (Instrument Limits)

An Open Lead Curve, as the name suggests, does not substitute any electronic components for the cell. For instructions on the measurement of the Open Lead Curve on your system, see the App

Note section on the Gamry website. A typical Open Lead Curve for Gamry Instruments' Reference 600 is shown in Figure 5.

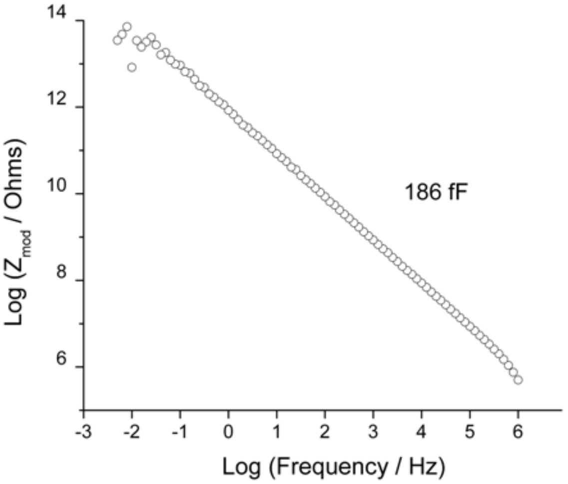

Figure 5. Open Lead Curve for Gamry's Reference 600 Potentiostat. The curve was generated by Potentiostatic EIS (100 mV rms). The standard 60 cm cell cable was used.

Measuring this Open Lead Curve is a first step in evaluating your instrument. This capacitance is the lowest measurable value of the instrument. An approximation of an instrument's accuracy is that a decade larger value is measured with 10% error and a decade larger than that with 1% error. However, this estimation is not as reliable as the method of direct measurement described earlier, using known electrical components to evaluate the accuracy.

The object of measuring the Open Lead Curve is to identify the absolute limits of the system; therefore, any user evaluating this curve should use standard good practice. As stated earlier, the leads themselves can act as a capacitor. To isolate these plates, the Reference and Counter leads are shorted and placed outside of a Faraday Cage. The Working and Working Sense leads are shorted and placed inside the Faraday Cage.

> *Note, the Open Lead Curve is the limit that the system can measure…it says nothing about how accurately the system can make a measurement at this limit.*

With Gamry Instruments' Reference 600, the capacitive limit (Limit B) is about a decade higher than the instrument's Open Lead Capacitance. Limit B is shifted to the lower-left due to the inverse relationship of capacitance with impedance and frequency. This instrument has a "real" capacitance that lives inside the instrument of about 180 fF. This is the instrument's Open Lead Capacitance. Therefore, no experimental design will allow you to measure a capacitance of a cell that is less than this value. An instrument's Open Lead Capacitance contributes to, *but does not determine*, the value of the capacitive accuracy limit (Limit B). Figure 5 is an example of an untrustworthy measurement.

Gamry software does not correct for this Open Lead Capacitance by a post-measurement offset, because this number has variability system-to-system and with cell lead placement (see above discussion).

Summary

This document describes the Accuracy Contour Plot as a tool to evaluate the ability of a given potentiostat to accurately measure different values of impedance at different frequencies.

Additional artifacts from the user's electrochemical cell may further limit the accuracy of the measurement. Depending on the properties of the system and parameters of the experiment, the potentiostat is capable of measuring a response that is a signature either of the user's cell (desired) or the hardware itself (not desired). Potentiostats of different models or from different manufacturers will have very different Accuracy Contour Plots.

©Gamry Instruments Copyright 2006 Rev. 1