Technical NOTE

GAMRY INSTRUMENTS

Accuracy Contour Plots – Measurement and Discussion

Purpose of This Note

This technical note discusses the Accuracy Contour Plot (ACP). The ACP gives the user valuable information about a potentiostat's EIS performance and accuracy. It allows the user to compare the EIS capability of any potentiostat.

Further, this document describes the different regions of an ACP and discusses its limits – including Open and Shorted Lead measurements. Additionally, it contains a general discussion for measuring Accuracy Contour Plots including advice how to set up cells and cable wiring for accurate results.

Introduction

Electrochemical Impedance Spectroscopy (EIS) is an indispensable, valuable, and versatile analytical tool for resolving electrochemical processes.

The impedance measurement is a collective representation of all components of a system – the cell, the instrument, and the connecting cables. However, instruments are not always capable of measuring the cell correctly. They are subject to restrictions which limit the range and the accuracy.

> If you need basic information on EIS, see Gamry's application note at **www.gamry.com**:
>
> **Basics of Electrochemical Impedance Spectroscopy**

Hence 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. You have to know the limits of your instrument.

The Accuracy Contour Plot shows the accuracy of a given EIS system. Researchers can use it to obtain the EIS capability in the region they are measuring a cell. The goal of this document is to provide the necessary tools to determine the limits of the instrumentation.

> Accuracy Contour Plots for the *Reference 600*, *Reference 3000*, and *Interface 1000* can be found under "Product Images" at **www.gamry.com**.

In this note, 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 next section of this technical note discusses the Accuracy Contour Plot and describes its different limits.

The Accuracy Contour Plot

Figure 1 shows a general scheme of an Accuracy Contour Plot. The graph is a log-log plot, fashioned as a Bode-type plot. The magnitude Z_{mod} of the impedance is plotted versus frequency f.
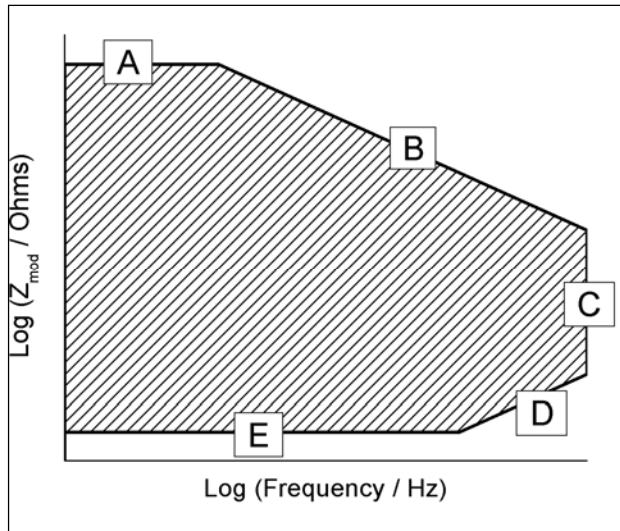
Figure 1 – Generic form of an Accuracy Contour Plot. For details, see text.

The hatched area indicates the region in which EIS measurements can be done in a specific accuracy. Beyond this region, measurements are untrustworthy as accuracy is highly uncertain.

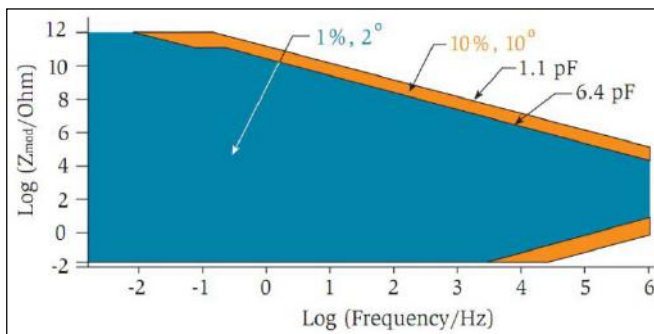Figure 2 shows the Accuracy Contour Plot of Gamry's Reference 600.

Figure 2 – Accuracy Contour Plot for Gamry's Reference 600.

The ACP in Figure 2 shows two different colored areas. Both are assigned to a specific accuracy limit.

- 1% magnitude / 2° phase shift
- 10% magnitude / 10° phase shift

Within these areas, EIS measurements can be performed with the designated accuracy. Further, two lines are tagged. Both represent the lowest measurable capacitance within a given accuracy and frequency range. For example, the Reference 600 is able to measure capacitances down to 6.4 pF with an accuracy of 1% magnitude / 2° phase between 0.3 Hz and 1 MHz.

The Accuracy Contour Plot covers a wide range of frequency and impedance. It contains the accuracy limits of EIS for a potentiostat. As potentiostats are multi-use instruments, scientists in different applications are concerned with the system performance in regions near different limits. The following sections describe these limits.

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 EIS region.

The manufacturer of a 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. The drift causes a random phase response, whereas an internal resistance causes the phase to approach 0°.

Cell currents in the region near this limit are exceedingly low. For example, we assume that a sample has an impedance of 10^{12} Ω. A typical 10 mV AC signal is only passing 10^{-14} A – this is only 10 fA!

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

Limit B – lowest measurable capacitance

This region represents the accuracy limit for the low-capacitance capability of an instrument. The value of this capacitive limit is a concern to scientists evaluating **semiconductors**, **dielectrics**, or **organic coatings** (e.g. paints on metal substrates with good barrier properties). The thicker the coating, the lower is its capacitance.

In the Bode plot, capacitors are represented by a line with slope equal to -1, determined by the relationship of capacitance C, frequency *f*, and magnitude Z_{mod} of

the impedance (see Equation 1). The phase shift for ideal capacitors is -90°.

$$Z_{mod} = -\frac{1}{\omega C} \qquad \text{Eq 1}$$

ω is the angular frequency and is equal to $2\pi f$.

Smaller capacitance values shift the line towards the upper right (away from the origin). Larger capacitances shift the diagonal line towards the lower left.

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 guideline for the trustworthiness of a measurement.

Limit C – maximum measurable frequency
This line represents the limiting frequency of an AC signal. The potentiostat's manufacturer specifies it 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.

A high proportion of electrochemical cells have impedance values within this range.

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 a slow response of the Reference Electrode (remember, at 1 MHz the cell has to respond to a million sine waves in the span of 1 s).

Additionally, several instrumental factors can affect measurements taken at Limit C, such as the slew rate (description of how fast an Op-Amp can respond to a change in input) or the frequency response of single components.

Limit D – low impedance at high frequency
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**.

Inductive signatures may appear in a user's impedance spectrum in the region near this limit. In a typical Nyquist plot, the curve extends below the x-axis. In a Bode plot, inductive signatures lead to a +90° phase shift. The magnitude appears as a straight line with a slope equal to +1.

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.

Inductance describes a magnetic flux due to current flowing through a wire. Inductive pickup or influence occur 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.

The position of Limit D is specified by giving the value of the inductor that has the same Bode plot as Limit D.

Limit E – lowest measurable impedance
Analogous to the discussion of the 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 A!

However, if this exceeds the maximum current rating of the potentiostat, the impedance can not be measured, even with poor accuracy. By decreasing the excitation level, the current signal can be decreased.

The absolute limits – Open and Shorted Lead

The Accuracy Contour Plot gives the user information what accuracy can be reached at different EIS measurements. However, the ACP does not show the maximum EIS capability of an instrument. There is still a region beyond the ACP limits.

The maximum EIS capability of an instrument can be determined by Open and Shorted Lead measurements. Both measurements give the absolute EIS limits. Beyond these limits no cell can be measured.

Figure 3 shows the Open Lead and the Shorted Lead measurement of a Reference 600.
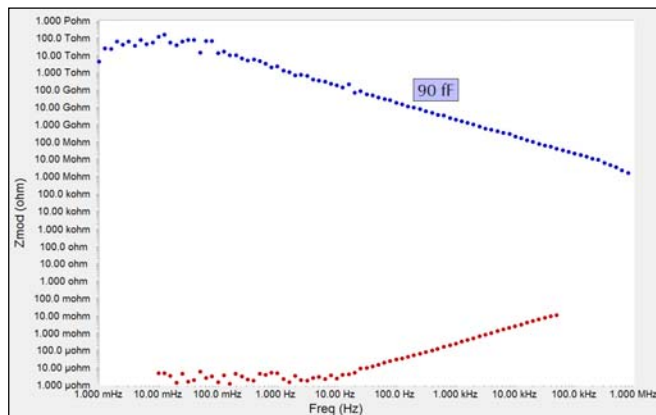

Figure 3 – Magnitude-only Bode plots of an (●) Open Lead and a (●) Shorted Lead measurement on a Reference 600. For details, see text.

A potentiostatic EIS experiment was performed to obtain the Open Lead curve. DC voltage of zero and an AC voltage of 50 mV$_{rms}$ were applied. The Shorted Lead curve was obtained by a galvanostatic EIS experiment using zero DC current and 300 mA$_{rms}$ AC current. A standard 60 cm cable was used for both tests.

As both measurements are at the limits of the instrument, the setup of the cell cables has to be carefully arranged for correct results.

The Open Lead and Shorted Lead curves give the absolute limits that an instrument can measure. Both curves contribute to, but do not determine, the value of accuracy.

In contrast, the Accuracy Contour Plot shows how accurately the system can make a measurement.

Open lead

The Open Lead measurement simulates infinite impedance between the cell leads. It gives information about the maximum measurable impedance and minimum measurable capacitance of a system. The curve is beyond (further top right) the Limits A and B of an Accuracy Contour Plot.

The Open Lead curve in Figure 3 (blue curve) reveals a maximum measurable impedance between 10 TΩ and 100 TΩ (10^{13} Ω - 10^{14} Ω!).

The minimum measurable capacitance is about 90 fF for the Reference 600 when using the parameters mentioned above. Hence no experimental design will allow you to measure a capacitance of a cell that is less than this value.

Gamry software does not correct for this Open Lead capacitance by a post-measurement offset because this number has variability system-to-system and depends on the cell lead placement (see later discussion).

Shorted lead

The Shorted Lead measurement – as the name already says – simulates a shorted configuration of the cell leads. It obtains the lowest measurable impedance of a system. In an Accuracy Contour Plot, it is beyond (further bottom right) the Limits D and E.

The Shorted Lead curve of the Reference 600 in Figure 3 (red curve) shows a lowest measurable impedance between 1 µΩ and 10 µΩ at frequencies below 10 Hz.

Above this frequency inductive effects lead to a slight increase in impedance. This is an effect of inductive artifacts that arise from magnetic fields from the cell cables. Later discussions show how to minimize these effects.

Measuring Accuracy Contour Plots

Open and Shorted Lead measurements give a first impression about the instrument's EIS capability. However, to know the accuracy of an EIS system, the Accuracy Contour Plot is needed.

The following sections describe what is needed to measure an Accuracy Contour Plot – for any computer-controlled potentiostat. A discussion follows about the correct cell setup including advice to researchers using EIS to study different applications.

Getting started

To record an Accuracy Contour Plot, the response of idealized cells (resistors and capacitors) is evaluated.

These cells should cover a wide impedance range between the Open and Shorted Lead curves.

For example, ACP measurements for Gamry's Reference 600 were done with following parts:

- Resistors between 1 TΩ and 10 mΩ in steps of one decade
- Ceramic capacitors between 10 pF and 100 μF

Potentiostatic EIS measurements are executed with each resistor and capacitor. For this, DC voltage is set to 0 V and AC voltage to 10 mV$_{rms}$. The AC voltage has to be reduced when measuring very low resistances if the current exceeds the instrument's limit.

All EIS measurement should be performed in "*Low Noise*" mode. The instrument has to be calibrated.

Note that the Accuracy Contour Plot strongly depends on the setup (see also section "Good electrochemical practices"). Gamry typically measures its Accuracy Contour Plots with a standard 60 cm cable. Hence the resulting ACP is only valid for this cable. Varying cable lengths and setups can lead to significantly different results.

Evaluation

As mentioned before, several single measurements have to be recorded for getting a whole ACP. This section describes how to evaluate a single measurement to create a whole ACP. Figure 4 shows an example of a potentiostatic EIS measurement on a 1 MΩ resistor.
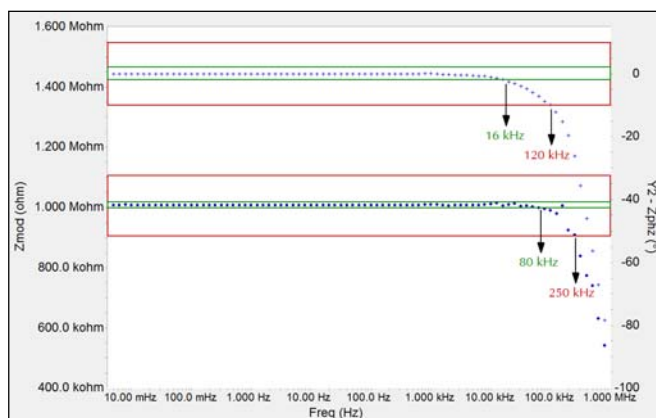

Figure 4 – Bode diagram of a potentiostatic EIS measurement on a 1 MΩ resistor measured with the Reference 600. (●) magnitude, (+) phase, (●) 1% – 2° limit, (●) 10% – 10° limit. For details, see text.

The Accuracy Contour Plot requires the frequencies where the accuracy limits are exceeded. As discussed earlier (see Figure 2), Gamry uses two different accuracy limits for its Accuracy Contour Plots – 1% magnitude/ 2° phase and 10% magnitude/ 10° phase.

First, the correct cell-parameter of the resistor or capacitor respectively has to be found by fitting the curve. Afterwards, the specific frequencies are marked where the impedance exceeds the 1% and 10% accuracy limit.

The same is done with the phase curve. The one specific frequency is marked where phase varies more than 2° and 10° from its ideal. For resistors this value is 0° and for capacitors -90°.

In Figure 4, all four frequencies are highlighted for the 1 MΩ resistor. For the ACP only one value for each accuracy limit is needed. Hence the points 1 MΩ/16 kHz and 1 MΩ/120 kHz are used in the ACP.

This procedure is done with each single resistor and capacitor. All resulting points for both accuracy limits are then connected with each other, forming the ACP.

As a wide range of cells is being measured at their limits, accurate cell setups are important. The following section gives detailed information about the correct cell setup and cable wiring. These should be also kept in mind when studying different applications.

Good electrochemical practices

The Accuracy Contour Plot gives the user a complete overview about the accuracy of EIS measurements of a potentiostat. It covers all regions that occur also in real systems – high-impedance, low-capacitance, and low-impedance.

To ensure high accuracy and integrity, all Gamry potentiostats use a Working Sense (WS) lead to measure and control the potential difference versus the Reference Electrode (RE). A separate Working Electrode (WE) lead is used 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.

However, wrong cabling and wrong test setups can make the Accuracy Contour Plot and other measurements obsolete. Hence, this section contains a general discussion (including advice for correct measurements) for scientists evaluating systems that

fall into the previously mentioned regions near the different limits.

High-impedance systems (Limit A)

One of the assumptions of EIS theory is that the system has to be linear. In general, this assumption is maintained by applying a small excitation amplitude (such as a default value of 10 mV$_{rms}$). 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 as similar currents are passed.

> Caution, large amplitude excitations may change the sample. Hence the assumption of linearity could not be valid anymore. Use with care.

High-impedance samples, by definition, only pass small currents, which are easily swamped by noise. A Faraday cage will improve the reliability of results from a high-impedance sample at typical AC amplitudes.

A Faraday cage is a grounded conductive shield that encases the test cell. The continuity of the conductive path of the cage is crucial. It blocks external electrostatic interferences (e.g. the line frequency at 50 or 60 Hz or radio frequencies) from being picked up in the leads. A general guideline is that a Faraday cage becomes important at currents below 100 nA.

> If you need more information about the Faraday cage, see Gamry's application note at **www.gamry.com**:
>
> **The Faraday Cage: What Is It? How Does It Work?**

Low-capacitance samples (Limit B)

When measuring cells with low capacitances, **stray capacitance** can affect the results.

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 parallel plates of a capacitor, with the air between them as the dielectric. This capacitance C is a function of the size A of the

clips (plates) and the distance d that separates them. This relationship can be approximated by:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d} \qquad \text{Eq 2}$$

ε_r is the relative permittivity which depends on the dielectric medium (about 1.00054 for air). ε_0 is the permittivity of vacuum (about $8.854 \cdot 10^{-12}$ F m^{-1}).

For example, using axially placed alligator clips separated by 2 cm with a surface area of about 2.5 cm^2. By using Equation 2, the calculated capacitance between both clips would be about 110 fF. This capacitive contribution would be in any measurement just from axially placed alligator clips. This capacitance is large enough to cause a finite phase shift.

To minimize this effect, the cell should be connected with radially placed (as opposed to axially) alligator clips, see Figure 5. This setup minimizes the effective size of the "plates" and reduces stray capacitance. The distance between the WE/WS pair and CE/RE pair should be maximized.

Figure 5 – Preferred orientation for alligator clips to minimize the capacitive contribution from the clips (optimized plate area).

> Note that also cell leads can contribute to stray capacitance. Hence Gamry's cell cables have driven shields to reduce capacitance of the leads.

Low-impedance systems (Limits D and E)

Mutual inductance determines Limits D and E. These limits depend on the influence of a magnetic field on the sense leads generated by the current-carrying leads.

The following practices described here are examples of experimental designs by informed scientists permitting the instrument to function to its maximum capability.

- Minimize the field

Remember, current is carried between the Working and Counter Electrode which induces a magnetic field. Figure 6 illustrates this effect.
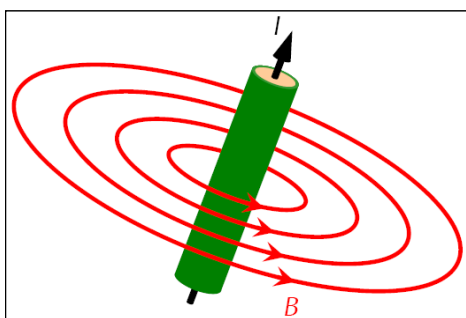

Figure 6 – Schematic diagram showing an electrical conductor with flowing current *I* and the induced magnetic field *B*.

This relationship is based on Biot-Savart's law where the induced magnetic field *B* is proportional to the applied current *I* and inversely proportional to the distance from the conductor.

In college, this rule is also known as "right-hand-rule" or "corkscrew-rule". The thumb points in the direction of the conventional current (plus to minus). The fingers point in the direction of the magnetic field.

The radiated external field can be minimized by physically twisting WE and CE leads as current is being carried in opposite directions in both leads – the thumb is pointing in opposite directions.

- Minimize the pickup

As discussed above, WS and RE control and measure the potential. Hence it is the pickup of the inductive field in the RE/WS pair generated by current flowing through the WE/CE pair that limits the EIS performance in the high-frequency low-impedance region.

By keeping both sense leads (RE and WS) close together, they "sense" 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 sense leads as it ensures they remain in proximity.

> Significantly lower inductances can be achieved by using Gamry's special ***Low-Impedance cell cable*** (P/N 990-00239).

- Arrange the pair

The properties that we witness are the fundamentals of a transformer. As discussed above, by tightly twisted WE/CE and WS/RE pairs the induced magnetic fields and the pickup by the sense leads can be minimized.

Further, the distance between the current-carrying and the sense pairs should be maximized. Each pair should extend radially from the potentiostat and then approach the cell from opposite directions (180°), as shown in Figure 7.
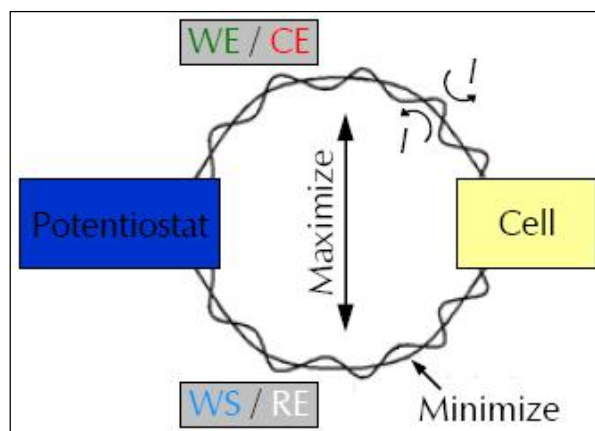

Figure 7 – Diagram of recommended cable positioning to study a low-impedance sample. For details, see text.

Remember, trade-offs and limits exist in most experimental designs. While maximizing the distance between the twisted sense and current-carrying cell lead pairs to minimize mutual inductance, it will increase stray capacitance between the WE/WS and CE/RE pairs.

Summary and Discussion

This technical note discusses the limits of an instrument's EIS capability. The Accuracy Contour Plot gives the user valuable information about the accuracy of an EIS system in a wide impedance and frequency range. It shows the user if an EIS measurement is reliable and trustworthy.

Open Lead and Shorted Lead measurements complement the ACP by showing the absolute EIS limits of an instrument.

Additionally, this document includes a field guide, what is needed to measure an ACP on your own and how it is done – for any computer-controlled potentiostat.

Finally, this note discusses different ways of cell and cable setups to optimize an instrument's measurement capability at the limits of an Accuracy Contour Plot. It gives the user most helpful advices that are useful for different kinds of applications and measurements.

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