Accuracy Contour Plots and EIS Accuracy

Written by Alexis Gray, PhD | alexis@admiralinstruments.com

This application note discusses how to use an Accuracy Contour Plot (ACP) to evaluate the EIS performance of a potentiostat. The process Admiral Instruments uses to generate our ACPs is also described.

Electrochemical Impedance Spectroscopy (EIS) is a versatile and central technique in the realm of electrochemical analysis. By probing the impedance response of electrochemical systems across a range of frequencies, EIS offers insights into complex processes spanning from corrosion studies to battery characterization.

However, the reliability and relevance of conclusions made using EIS data hinges upon the accuracy of the impedance measurements and an understanding of how sampling parameters and experimental setup can influence the results. Therefore, it is vitally important to understand the specifications and limitations of the EIS-capable instrument you are using. This application note provides insights into interpreting an instrument's capability to perform EIS through the study of the instrument's Accuracy Contour Plot (ACP).

This application note assumes a basic understanding of EIS and impedance (Z). To learn more about these concepts, please read the application note Introduction to Electrochemical Impedance Spectroscopy (EIS) on our website.

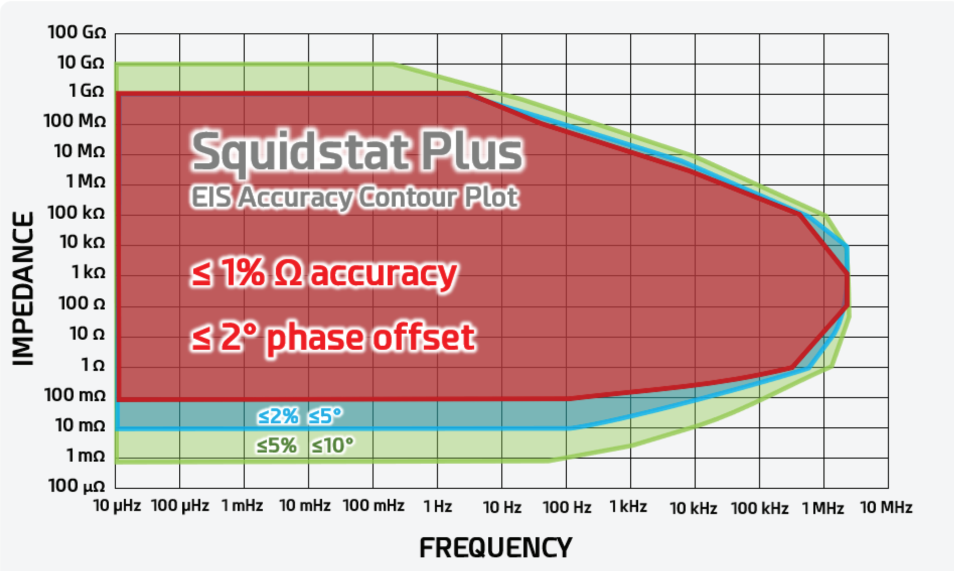
The Accuracy Contour Plot

An Accuracy Contour Plot (ACP) is a graphical representation of an instrument's ability to measure impedances across a range of frequencies and well-defined sampling parameters. An ACP is the definitive way to communicate the expected accuracy of EIS measurements for users to identify regions of high accuracy and pinpoint potential sources of measurement error.

Figure 1 shows an example Accuracy Contour Plot of a Squidstat Plus potentiostat from Admiral Instruments. The logarithm of impedance is plotted on the y-axis as a function of the logarithm of frequency. Measurements in the shaded region are guaranteed within a specific accuracy. Three different color contour lines on the plot indicate different levels of measured impedance accuracy and phase offset:

- Red – 1% measured accuracy, 2° phase offset
- Blue – 2% measured accuracy, 5° phase offset
- Green – 5% measured accuracy, 10° phase offset

Within the shaded regions, EIS can be performed to within the accuracy specifications. But any attempted EIS measurements made at frequencies outside the shaded region should not be considered accurate, even if values are recorded as part of the measurement.



Sampling Parameters

- 100 uOhm to 10 GOhm precision resistors
- Cable length: 100 cm
- Signal amplitude: ≤10 mV peak-to-peak
- Signal amplitude: 1 A peak-to-peak for impedances ≤5 mOhm

Color Codings

The RED, BLUE, and GREEN areas show accuracy within percent (%) impedance and degrees (°) phase offset:

RED: 1%, 2°

BLUE: 2%, 5°

GREEN: 5%, 10°

Figure 1. Accuracy Contour Plot for a Squidstat Plus unit. The three contour lines represent three different degrees of accuracy: measurements in red are guaranteed within 1% measured impedance accuracy or 2° phase offset, blue within 2% or 5°, and green within 5% or 10°.

As an example, consider a cell with an impedance of 1 Ohm. According to the ACP in **Figure 1**, impedance accuracy and phase offset is guaranteed within 1%/2° up to 250 kHz, 2%/5° up to 500 kHz, and 5%/10° up to 1.1 MHz. Above 1.1 MHz, accuracy is significantly reduced, emphasizing the importance of staying within the specified frequency range for reliable measurements.

Beyond assessing the graph, the sampling parameters used to generate the plot are equally significant in gauging EIS accuracy through an ACP. Parameters such as cable length and AC excitation amplitude play a critical role in the signal response and, consequently, the overall accuracy of impedance measurements. Clearly communicating these parameters ensures the reproducibility of experiments and facilitates accurate interpretation. For example, one of the basic requirements of EIS is linearity; that is, the signal response to an applied AC excitation amplitude is supposed to be linear and therefore representative of a stable unchanging system. For a resistor, this linearity requirement is true for all practical excitation amplitudes. Higher excitation amplitudes can lead to a more pronounced signal response and, often, an aesthetically superior ACP. However, according to Butler-Volmer kinetics and electrochemical theory, current-voltage response is inherently always nonlinear for non-ideal real electrochemical systems, yet it can be assumed linear when the applied amplitude and response are limited to a few millivolts. If the excitation amplitude used to generate the ACP exceeds real-world norms, the ACP might suggest better accuracy than practical scenarios, emphasizing the importance of listing and understanding sampling parameters for meaningful interpretation.

Limiting Regions in an ACP

Figure 2 shows a more general Accuracy Contour Plot with labels for each limiting region, which are described in this section in detail.

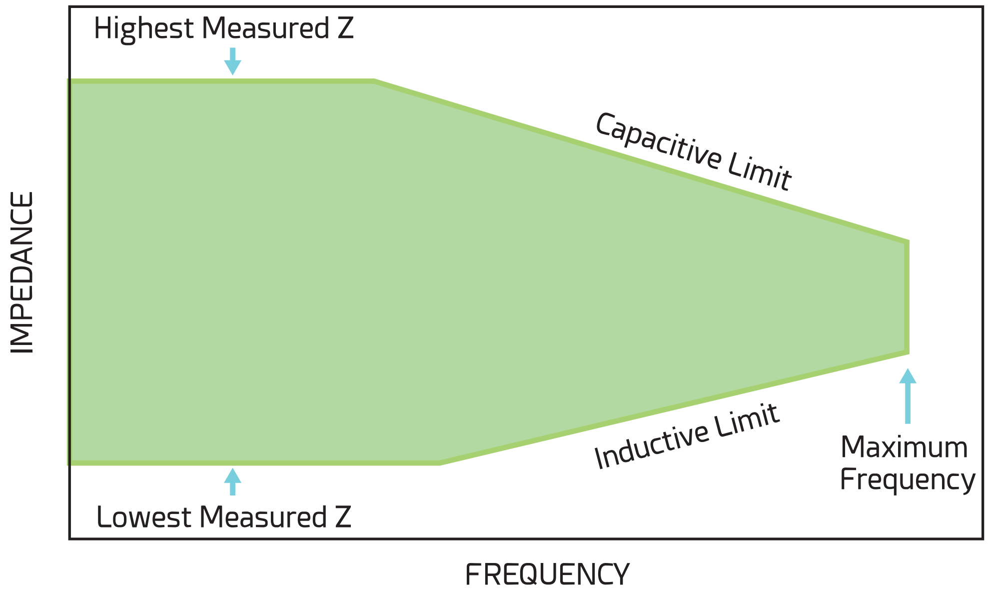


Figure 2. *The five limiting regions on an Accuracy Contour Plot: the highest and lowest measurable impedances (Z), the capacitive limit, the inductive limit, and the maximum frequency limit.*

Measurable Impedance Limits

The two horizontal lines represent the highest and lowest measurable impedances (Z). These limits are largely controlled by the current limitations of the instrument. To accurately measure high impedances, the instrument must be able to accurately measure low currents with high precision. Thus, the accuracy of the lowest current range plays a large role in the highest measurable impedance limit.

To accurately measure low impedances, the current excitation amplitude must be high enough and stable to yield a voltage response from the cell sufficient for the instrument to detect accurately. A few millivolts is the widely accepted voltage amplitude response which does not violate the condition of linearity; that is, the amplitude is small enough that the response can still be assumed to be linear in accordance with Butler-Volmer kinetics. However, this is a general guideline and may not be true for all systems. Thus, the maximum current output, the accuracy of the highest current range, and the sensitivity of the instrument in detecting and resolving small AC voltages are the primary limiting factors for the lowest measurable impedance limit.

Maximum Frequency Limit

The maximum measurable frequency gives the range of impedances which can be accurately measured at the highest advertised EIS frequency. This limit is primarily defined by the bandwidth of the electrometer and the bandwidth of the ammeter. In simple terms, the electrometer inside a potentiostat measures the voltage between the working sense lead and the reference lead, and the ammeter measures current. The bandwidth determines how quickly the electrometer and ammeter can measure changes in the input signal. A higher bandwidth means the potentiostat can measure and respond to signals faster, and therefore can accommodate higher frequencies. Thus, the high frequency limit is largely dictated by the bandwidth of these components. For example, the Squidstat Plus advertises a highest measurable frequency of 2 MHz, which is the bandwidth of the electrometer. The bandwidth of the ammeter depends on which current range the instrument is in; the least sensitive current ranges also have a bandwidth of 2 MHz, but the more sensitive current ranges, which measure higher impedances (ranges with nA-μA sensitivity) have a lower bandwidth. In addition to capacitive effects, this lower bandwidth can impact the highest impedance which can be measured at the maximum frequency limit.

The Capacitive Limit

The capacitive limit is primarily determined by stray capacitance, or the unwanted buildup of charge on components outside the system of interest, such as cell cable leads, typically caused by their proximity to one another. This region in the ACP is of interest when studying mid-to-high impedance systems at higher frequencies, such as semiconductors and dielectric coatings. In the context of electrochemical measurements, the overall circuit is comprised of the potentiostat, the cable, and the device under test (DUT) to which the cable is connected. The stray capacitance affecting internal components is minimal compared to the stray capacitance experienced by the cable and the DUT. The cable is susceptible to stray capacitance between the individual leads and between the leads and ground. Cable length also plays a significant role, as longer cables have increased area available for stray capacitance. This is why it is important that the cable length used to generate an ACP is listed as part of the sampling parameters. If a shorter cable is used, the ACP will be better.

While stray capacitance cannot be entirely removed, the effects it can have on electrochemical measurements are partially corrected for during the calibration process. Each Squidstat Plus, Penta, Decka, and Venta is calibrated and quality checked using the specific channel cable set assigned to it. These cables should not be exchanged for other cables without first performing a recalibration. This ensures that the cable length, cable shielding, and small differences between individual cables caused by variations in manufacturing are accounted for. Other sources of stray capacitance such as environmental factors or from the DUT cannot be accounted for during calibration but can be mitigated with good electrochemical practices, such as adding shielding around the DUT or using a specialized test fixture designed to mitigate stray capacitance.

The Inductive Limit

The region referred to as the inductive limit is determined by common mode voltage and inductive effects. This region of the ACP is of interest when studying low impedance systems at high frequencies, primarily applicable for battery and fuel cell research. Simply put, common mode voltage is voltage seen by both inputs to a differential amplifier. **Figure 3** below shows a differential amplifier with two voltage input signals (V_1 and V_2) and one voltage output (V_{out}).

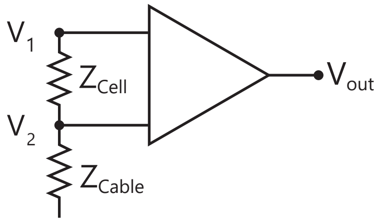


Figure 3. *A basic differential amplifier circuit with two voltage inputs V_1 and V_2 and one differential voltage output V_{out}. The inputs are connected to either side of a cell with an impedance Z_{Cell}. Both voltage inputs see a common mode voltage error contribution from the impedance of the cabling, Z_{Cable}.*

The equation for V_{out} is given by:

$$V_{out} = V_1 - V_2 + a^*V_{cm}$$

The term a^*V_{cm} is a frequency-dependent error term associated with common mode voltage error, where V_{cm} is the common mode voltage and a is a scalar, representing imperfections in the circuitry. Since the difference between the signals is taken, the common mode voltage seen by both V_1 and V_2 is mostly filtered out. The scalar a is the extent to which it cannot be filtered out. High precision circuits such as those used in research-grade potentiostats like our Squidstats will have a low a.

In this context, the input signals V_1 and V_2 are from the reference (RE) and working sense (WES) leads, and the difference between them is the voltage of the electrochemical cell, which has an impedance Z_{Cell} that is of interest. The cabling also has an impedance, Z_{Cable}, which is composed of two components: the impedance of the cable itself (approximately a few milliohm), and a variable inductive component caused by inductance. Z_{Cable} is not part of the system being measured, and it contributes to common mode voltage. If there are external cables connecting the leads to the DUT, then the impedance of those external cables, which also have a variable inductive component, increase Z_{Cable}. Thus, to reduce the effects of cabling, it is recommended to reduce or eliminate any external cabling between the potentiostat leads and the connection terminal on the cell.

Mutual inductance occurs when the changing magnetic field (**B**) produced by current (**I**) flowing through one set of leads induces a voltage in another set of nearby leads. In the context of potentiostat measurements, sense leads that are responsible for controlling and measuring the potential can be affected by the magnetic field generated by the current-carrying leads.

When current flows through the working electrode (WE) and counter electrode (CE) leads, a radial magnetic field is generated around these current-carrying leads, which is illustrated in **Figure 4**.

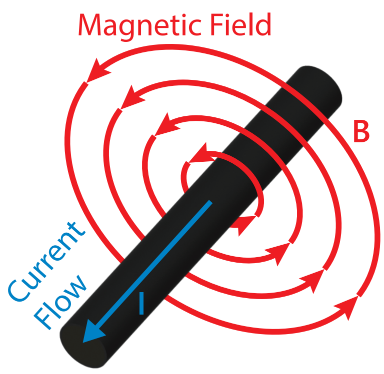


Figure 4. *Magnetic field (**B**) induced by current (**I**) flowing through a cable.*

The changing magnetic field produced by the current flowing through WE and CE induces a voltage in the sense leads and external cabling, due to inductance. This induced voltage is an unwanted common mode voltage that can interfere with the accurate measurement of the potential. However, by twisting the CE and WE, the direction of the magnetic field in both leads opposes one another, thereby reducing the effect it has on the sense leads. Additionally, the sense leads should be as far from the current carrying leads as possible, but close to each other so that they experience similar magnetic fields from the mutual inductance of the WE and CE pair. By keeping the leads in proximity, the differential amplifier can treat the induced voltage as part of the common mode voltage signal, partially compensating for its impact.

In the context of high-frequency EIS, the interference caused by inductance and common mode voltage can limit the performance of the system in the inductive region, particularly when studying low-impedance samples. In cases where Z_{Cell} is significantly lower than Z_{Cable}, the error term a*V_{cm} will have a higher impact on V_{out}.

Below is a summary of strategies described in this section to reduce common mode voltage error and the effects of inductance:

- The magnetic field can be partially compensated for by twisting the current carrying leads. Doing so causes the induced magnetic fields on the WE and CE cables to oppose one another, reducing its overall size and impact on the sense leads.

- Maximize the distance between the sense leads and the current-carrying leads while keeping the sense leads close to each other, enabling the differential amplifier to partially compensate for induced voltage as part of the common mode signal.

- Reducing or preferably eliminating external cabling between the potentiostat leads and the DUT will reduce Z_{Cable} and ultimately V_{cm}.

Generating an Accuracy Contour Plot

Most, but not all, companies manufacturing EIS-capable potentiostats and related instruments will provide ACPs for the instruments they sell. However, it's important to note that these plots do not necessarily reflect the performance of individual instruments shipped to users; instead, they represent an average of expected performance for a specific model. Admiral Instruments is unique in our industry to generate and share individualized Accuracy Contour Plots as part of the final calibration report with every single EIS-capable instrument that ships to our customers. **Figure 5** below is an example of such a report for a Squidstat Plus potentiostat. The following section covers the process for generating the ACP, using the Squidstat Plus as an example.

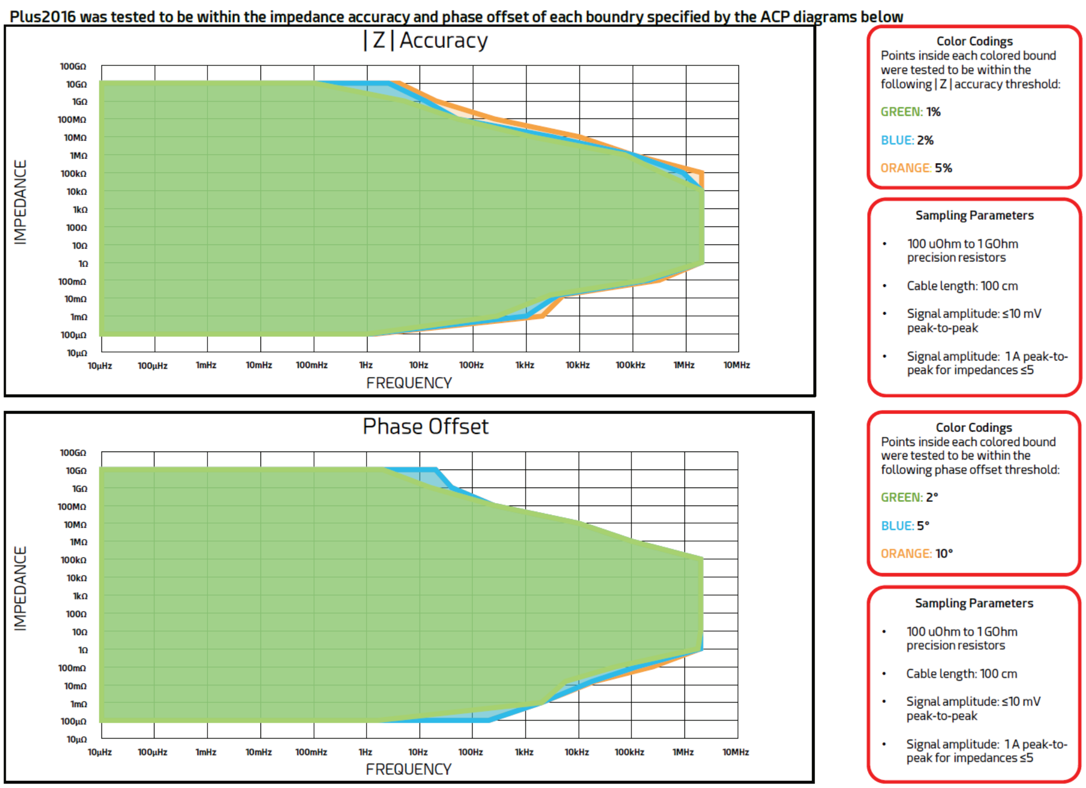


Figure 5. *Calibration report for a Squidstat Plus unit. Two ACPs are generated in each report: one for impedance accuracy and one for phase offset.*

The Procedure

This section describes the process that Admiral Instruments uses to generate ACPs to provide a comprehensive and transparent understanding of our process. Keep in mind that other potentiostat manufacturers employ their own unique methods for calibration and Accuracy Contour Plot generation.

Since the ACP is strongly dependent on setup, the standard 1 m cable calibrated with and assigned to the unit is used to generate each plot. If a different cable was used, the results could vary significantly. Each ACP is generated with 15 different resistors ranging from 100 µOhm to 10 GOhm, logarithmically spaced, using good electrochemical practices. The low impedance EIS measurements (100 µOhm, 1 mOhm, 15 mOhm, and 100 mOhm) are run on coaxial resistors with low self-inductance. The remaining resistors are placed inside a Faraday cage.

The Squidstat ground port located on the back of the instrument is connected to the Faraday cage to reduce noise from other electronic devices and stray capacitances. Galvanostatic EIS (GEIS) is used for evaluation of the 100 µOhm and 1 mOhm resistors while Potentiostatic EIS (PEIS) is used on the remainder. The EIS parameters for each resistor are listed in **Table 1** below. As mentioned previously, for resistors, the linearity assumption is true for all practical excitation amplitudes. Therefore, the excitation amplitude for each resistor was chosen to maximize the signal-to-noise ratio and mimic conditions used on real non-ideal systems.

Resistor Value	EIS Type	Excitation Amplitude	Starting Frequency (Hz)	Ending Frequency (Hz)	Steps per Decade
100 µOhm	GEIS	1 A	1	200	20
1 mOhm	GEIS	1 A	1	2000	20
15 mOhm	PEIS	1 mV	10	2e4	20
100 mOhm	PEIS	10 mV	10	2e6	20
1 Ohm	PEIS	10 mV	100	2e6	20
10 Ohm	PEIS	10 mV	100	2e6	20
100 Ohm	PEIS	10 mV	1000	2e6	20
1 kOhm	PEIS	10 mV	1000	2e6	20
10 kOhm	PEIS	10 mV	1000	2e6	20
100 kOhm	PEIS	10 mV	10	2e6	20
1 MOhm	PEIS	10 mV	1	1e5	20
10 MOhm	PEIS	10 mV	1	1e4	20
100 MOhm	PEIS	10 mV	0.1	250	10
1 GOhm	PEIS	10 mV	0.1	40	10
10 GOhm	PEIS	10 mV	0.1	40	10

Table 1. *The EIS parameters used for each resistor value to generate the Accuracy Contour Plot as part of the quality check process for the Squidstat Plus.*

Evaluating the EIS Data and Generating the ACP

After all data has been collected, the raw EIS data for each resistor is analyzed to determine at which frequencies the accuracy limits have been exceeded. First, the impedance data is fitted to a characterization curve for the specific resistor used. The characterization curves are generated for each resistor using a high-precision NIST-traceable LCR meter, which stands for the properties that it measures: inductance (L), capacitance (C), and resistance (R). Like all electronic components, real resistors exhibit capacitance and inductance as frequency-dependent parasitic properties, which cause the resistance to deviate from the labeled value, specifically at high frequencies. Thus, in addition to measuring the true resistance of a given resistor, the LCR meter gives a comparison characterization curve that measures how the resistance changes with frequency. The EIS data collected by the Squidstat is compared to this curve, and the frequencies at which impedance accuracy deviates from the curve at 1%, 2%, and 5% are noted and used in the ACP. The same process is repeated for the phase shift.

As an example, **Figure 6** shows a Bode plot of impedance as a function of frequency for the 100 kOhm Potentiostatic EIS sweep. The impedance values have been normalized with respect to the characterization curve for the resistor. The frequencies corresponding to 1%, 2%, and 5% impedance accuracy are visualized on the graph as horizontal lines. The graph intersects these lines at 355 kHz, 630 kHz, and 1.12 MHz, respectively. These frequencies are plotted accordingly on the ACP for 100 kHz.

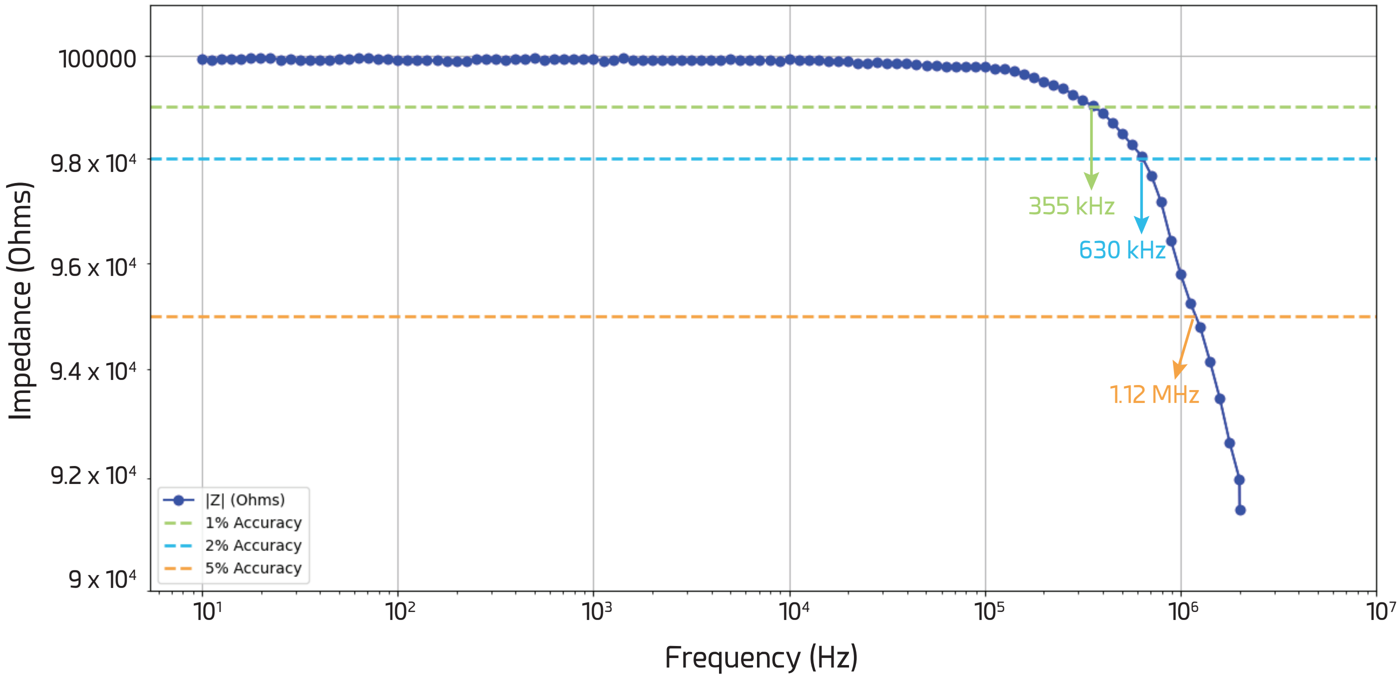


Figure 6. *A Bode plot of impedance as a function of frequency for the 100 kHz potentiostatic EIS sweep. The data has been normalized to the characterization curve. The intersection between the fitted EIS data and the horizontal lines corresponding to 1%, 2%, and 5% impedance accuracy give the corresponding frequencies used to generate the ACP.*

This evaluation is repeated for all 15 resistors, then the values are plotted and connected to generate accuracy contour plots for impedance accuracy and phase shift given in the calibration report.

Summary

This application note discusses how to interpret an Accuracy Contour Plot (ACP) to evaluate an instrument's EIS capabilities and limitations. The following key points were discussed:

- Accuracy Contour Plots allow users to identify regions where EIS accuracy is reduced based on the impedance of their cell, the frequency of the measurement, and clearly communicated sampling parameters.
- The limiting regions of the accuracy contour plot were identified and explained. Suggestions on how to improve the accuracy of impedance measurements at each of the limiting regions were described.
- The process to generate an ACP was described in detail. The method used by Admiral Instruments for the Squidstat Plus was used as a guide.