TechnicalNOTE

Verification of Low Impedance EIS Using a 1 mΩ Resistor

Introduction

Electrochemical Impedance Spectroscopy, EIS, is a very powerful way to gain information about electrochemical systems. It is often applied to new electrochemical devices used for energy conversion and storage (ECS), including batteries, fuel cells, and super-capacitors. EIS can be used in all stages of the development of new devices, from initial evaluation of half-cell reaction mechanisms and kinetics, to quality control of packaged batteries.

Increased use of ECS devices in higher power applications (such as electric vehicles) has led to development of devices having very low impedance. Unfortunately for practitioners of EIS, impedance of modern ECS devices is often so low that it often cannot be measured using laboratory EIS systems. Most commercial EIS systems do not work well when impedance is below 0.1 Ω.

If an EIS system can make a measurement on a low impedance system, how can you tell if that measurement is valid?

This Technical Note describes a series of EIS measurements made on a 1mΩ surface mount resistor. The very small dimensions of this resistor minimized cable-related inductance errors. The measurements verify that a Gamry Instruments system can accurately measure this low impedance.

The techniques used to make these measurements and post-experiment corrections can be used to verify the performance of any low impedance EIS system.

Experimental guidelines presented here should be helpful when testing physically larger ECS devices. Many of the problems encountered in testing a small resistor also occur in testing a battery or fuel cell.

If you're new to EIS, you might want to read Gamry Instruments' **Basics of EIS** before reading the rest of this Technical Note. It can be found in the **App. Note** section on www.gamry.com. Information found in this introduction to EIS will not be repeated here.

Mutual Inductance

The cell-cable and placement of the leads connecting to the cell can have a major effect on EIS system performance. A phenomenon known as mutual inductance can limit the ability of an EIS system to make accurate measurements at low impedances and high frequencies. Mutual inductance errors appear in the measured EIS spectrum as an inductor in series with the cell's impedance. This section describes mutual inductance and its effect on EIS measurements and offers practical suggestions for its minimization.

All high-performance EIS systems use a four-terminal connection scheme. The four leads that connect to the cell under test are grouped into two pairs.

- One pair of leads conducts the current between the cell and the system potentiostat. These leads will be called the "current-carrying leads".
- A second pair of leads measures the voltage across two points in the cell. These leads will be called the "sense leads".

The term mutual inductance describes the influence of the magnetic field generated by the current-carrying leads on the sense leads. In essence, the current-carrying leads are the primary of a transformer and the sense leads are the secondary. The AC current in the primary creates a magnetic field that then couples to the secondary, where it creates an unwanted AC voltage.

This effect can be minimized in a number of ways:

- Avoid higher frequencies.
- Minimize the net magnetic field generated by the current-carrying leads.
- Separate the current-carrying pair from the sense pair.
- Minimize pickup of the magnetic field in the sense leads.

Avoid High Frequency

Mutual inductance creates a voltage error given by:

$$Vs = M\, di/dt$$

Vs is the induced voltage on the sense leads, M is the coupling constant (with units of Henries), and di/dt is the rate of change in the cell current.

M depends on the degree of coupling and can range from zero up to the value of the inductance in the current-carrying leads. Assuming a constant amplitude waveform in the primary, di/dt is proportional to frequency.

The importance of the error voltage depends on its size relative to the true voltage being measured, which in turn is proportional to the cell impedance.

Mutual inductance errors appear in the measured EIS spectrum as an inductor of value M in series with the cell's impedance.

Minimize the Net Magnetic Field

A current passing through a wire creates a magnetic field with the field strength proportional to the current. Fortunately, passing the same current in opposite directions through adjacent wires tends to cancel the external field.

Two different wire arrangements are commonly used to minimize inductance and magnetic fields. The first is a coaxial cable; a central conductor is used to carry the current in one direction and a second conductor surrounding the first carries the current in the opposite direction. The second common arrangement is the twisted-pair; two insulated wires carrying current in opposite directions are twisted together.

Separate the Pairs

The magnetic field produced by a wire loses intensity as the inverse square of the distance away from the wire. Separating the sense wires from the current-carrying wires can dramatically reduce the magnetic coupling.

Twist the Sense Wires

The concept of a magnetic loop probe is useful in understanding why a twisted sense pair minimizes magnetic pickup. A loop of wire in a changing magnetic field will see a loop voltage proportional to the area of the loop.

Twisting the sense wires helps in two ways. First, the twisted wires are forced to lie close to each other, minimizing the loop areas. Secondly, adjacent loops pick up opposite polarity voltages, which results in cancellation.

Cabling Recommendations

Use coaxial cable or twisted pair for each pair of leads. The distance between the pairs should be maximized. Arrange each pair so that they approach the cell from opposite directions as shown in Figure 1.

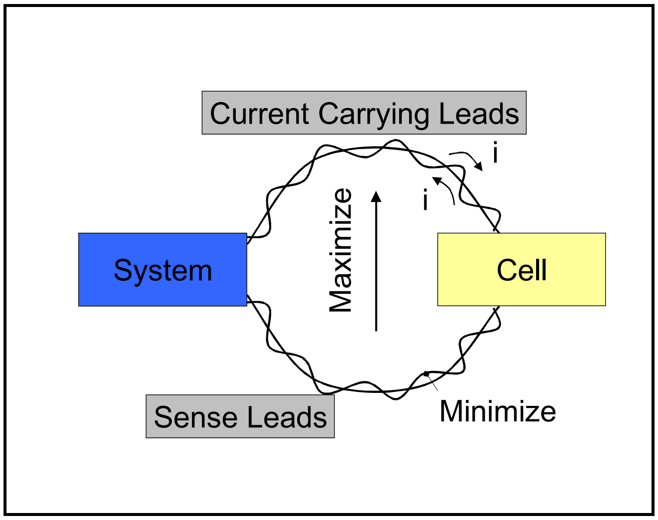

Figure 1. Recommended Cell Connections.

Mutual inductance errors are more significant at lower cell impedances and higher frequencies.

For example, on a system with 1 mΩ of resistance and 1 nH of mutual inductance, EIS phase shift will be 0.4° at 1 kHz and 3.6° at 10 kHz. If the resistance is lowered to 200 µΩ without changing the inductance, the phase shifts are 1.8° at 1 kHz and 17° at 10 kHz.

To minimize mutual inductance errors, Gamry Instruments has developed twisted-pair cell cables for our EIS systems. The results below show how these cables can improve the EIS spectrum of a test resistor.

Guidelines for Low Impedance EIS

These guidelines can greatly improve the accuracy of EIS measurements on low impedance cells:

- Use galvanostatic mode EIS.
- Use a large excitation current.
- Use twisted-pair or coax wiring.
- Use a mechanical fixture to insure reproducible cabling.
- A low impedance cell surrogate allows you to measure cable related errors.
- Subtract the surrogate's spectrum from the cell's spectrum to correct for cable errors.

Each of these will be discussed below. Experimental data will illustrate the importance of these guidelines.

Experimental

The Resistor

The 1 m Ω resistor used in these measurements is Part Number WSL20101L00FEA18 from Vishay.

This resistor was designed for surface mount PCB applications. It is an industry standard 2010 size with dimensions of approximately 5 mm long by 2.5 mm wide. Its accuracy rating is ± 5 % of its nominal value.

Vishay does not specify the inductance of this resistor. They do claim that the inductance of the WSL resistor family is between 0.5 nH and 5 nH and claim the family has "excellent frequency response to 50 MHz".

Electronics and Software

All experimental data were collected using a Gamry Instruments EIS300 EIS System built around a Reference 600 Potentiostat/Galvanostat/ZRA. In most of the tests, a Gamry Instruments Reference 600 Low Impedance Cell Cable, Gamry Part Number 985-81, was used in place of the standard cell cable.

The small size of the resistor makes direct connection between the resistor and the cell cable difficult and irreproducible. Four 2.5 cm long pieces of 30 AWG Tefzel insulated wire-wrap wire were soldered to the ends of the Low Impedance cell cable, the solder joints were covered with polyolefin heat shrink tubing and the small wires were twisted.

All tests were run using the Galvanostatic EIS script with zero DC current and 350 mA of excitation current. The peak-to-peak current is approximately 1 Ampere. Unless otherwise noted, the EIS frequency sweep began at 0.1 Hz and ended at 1 MHz. *Resistor Connections and Fixture*

Early experiments showed poor reproducibility. It was difficult to keep the connection and cell lead geometry constant when the resistor was changed.

This was addressed by building a fixture to hold the resistor in place. The fixture was based on a 30 mm long header with 4 mm lead spacing. This header was a standard commercial part from Samtec. The 0.5 mm square pins of this header are normally held in place by two plastic spacers.

The bottom side of the resistor was soldered to the middle of the header pins. At least 10 mm of header pin stuck out on either side of the resistor.

Once the resistor was in place, the plastic spacers were slid off of the header pins and the last 4 mm of each pin was bent at right angles. The pins were then inserted through holes in a piece of perforated fiberglass board, which held the assembly onto the board. Perforated fiberglass material is commonly used in electronics prototyping.

Only 2 mm of each twisted pair was untwisted when a Low Impedance cable was connected to this assembly. The pairs approached the assembly from opposite sides of the resistor. Each wire was soldered to the appropriate pin about 5 mm away from the resistor.

Once the wires were in place, they were taped to the board. This prevents changes in the lead geometry when the fixture is handled.

Resistor Surrogate

A resistor surrogate was built to have the same geometry and to connect to the EIS system in the same way as the resistor. It consisted of a 5 mm by 2.5 mm slug cut from 1.6 mm thick copper sheet.

It was soldered to the same fixture used for the resistor measurements. Figure 2 is a photograph of the connections between the surrogate and the Low Impedance Cell Cable. The fixture looks crude, but it gave reproducible results.

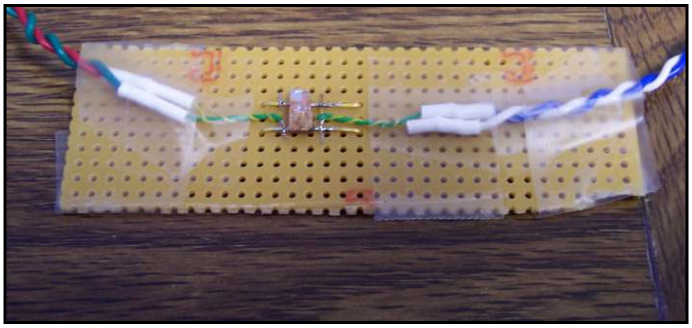

Figure 2. Surrogate Connected in Fixture.

Why Galvanostatic Mode?

Even though Potentiostatic EIS is the most commonly used EIS technique, it is poorly suited to impedance measurements of ECS devices.

This is why: current, voltage, and impedance are related through Ohm's Law. A voltage of 1 mV across 1 mΩ of impedance corresponds to 1 A of current. No commercial potentiostat is specified to control a typical ECS device's potential (0.5 V to 4.5 V) with < 1 mV of error. When a potential with a 1 mV (or larger) error is applied to a low impedance ECS device a very large DC current will flow. This current, given enough time, can alter a battery's state-of-charge.

Conversely, a galvanostat can easily control ampere currents to an accuracy of a few milliamps. The voltage on the cell is unaffected when the galvanostat is connected. The DC current is zero or some user defined value.

A modern EIS system with AC coupling or offset and gain in the voltage measurement can measure microvolts of AC voltage superimposed on a large DC voltage, as long as that voltage is stable.

Galvanostatic EIS is the preferred technique for EIS on ECS devices. This study employed Galvanostatic EIS to better model ECS measurements.

Why Use Large Excitation Currents?

In a galvanostatic EIS experiment, the voltage signal is proportional to the applied current. Measurement of voltages < 10 µV is difficult, since most measurement systems have a few µV of noise.

It is best if the AC excitation current is kept large enough that the AC voltage is >10 µV. For a 1 mΩ cell, this means the current must be 10 mA or greater.

Why Use Twisted Pair Wiring?

Figure 3 shows the importance of wiring in EIS measurement of the 1 mΩ resistor. There are two Bode plots overlaid in this graph. In all Bode plots, the dark colors are magnitude and the corresponding light colors are phase.

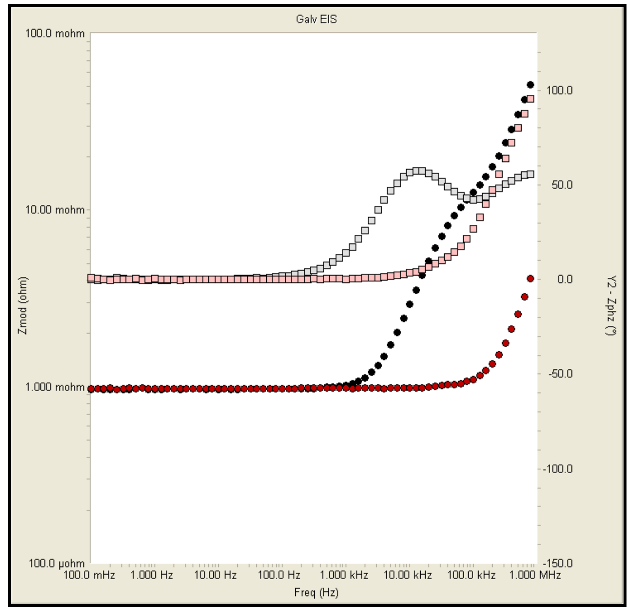

Figure 3. Resistor Spectra with Different Cables.

The black and grey data were recorded using the Reference 600's standard cell cable. Its alligator clips were clipped to the pins on the resistor/header assembly. The red and pink data were recorded with a Low Impedance cable for the Reference 600 connected as described above.

Both curves have similar shapes and low frequency impedance close to 1 mΩ. Both show inductance at higher frequencies. The inductance is much lower with the Low Impedance cable.

The Resistor Surrogate's Spectrum

Earlier graphs and discussion showed the importance of cabling on the measurement. But, even using a Low Impedance twisted pair cable, one doesn't know how much of the measured impedance is the true resistor impedance and how much to attribute to cable effects.

A resistor surrogate allows you to measure the cabling effects. The surrogate is a metal object with the same geometry and connection scheme as the resistor. Ideally it will have zero resistance and inductance.

The EIS spectrum of a copper slug used as a surrogate was recorded using the same fixture, wiring, and experimental conditions as the resistor test. Figure 4 shows Bode plots of the surrogate (in black and grey) and resistor spectra (in red and pink).

The surrogate spectrum is resistive at low frequencies and becomes inductive at higher frequencies. After removal of the point with an impedance below 1 μΩ, these data fit fairly well to a series RL model, with R = 4.5 μΩ and L = 444 pH.

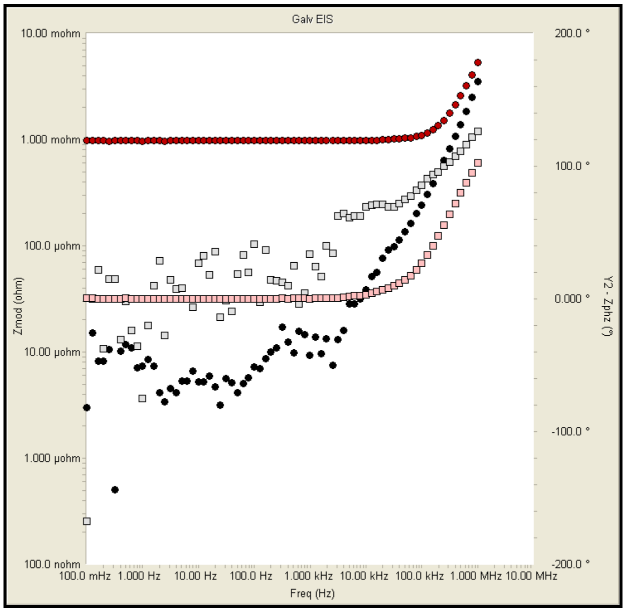

Figure 4. Resistor and Surrogate Spectra.

Is Spectrum Subtraction Useful?

Mutual inductance creates an error that shows up in an EIS spectrum as inductance in series with the cell's real impedance.

Similarly, an improper 4-terminal connection, in which current flows through both a current-carrying and a sense lead, can create resistive errors. This error is also in series with the cell's true impedance.

In our resistor tests, with a constant fixture and unchanging cell connections, these error should be identical in both the resistor's and resistor surrogate's spectra.

A series subtraction of the surrogate's spectrum from the resistor's spectrum can remove these effects.

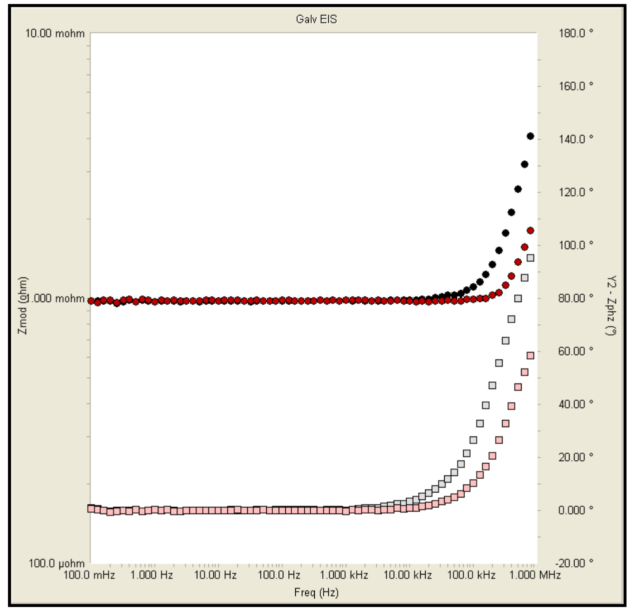

Figure 5. Corrected and Uncorrected Resistor Spectra.

Figure 5 shows the resistor's spectrum before (in black and grey) and after (in red and pink) a series subtraction of the surrogate's spectrum.

The resistive region in the corrected spectrum obviously extends to higher frequencies.

Spectrum Comparisons

There were three resistor spectra discussed above.

1. The spectrum using the standard cell cable.
2. The spectrum using the Low Impedance cable.
3. The spectrum using the Low Impedance cable corrected using surrogate data.

All of these spectra were fit to a series RL model. In the case of the data recorded with the standard cell cable only the data below 10 kHz were used in the fit., since the data above 10 kHz showed non-inductive phase shifts.

The R and L values resulting from the fits are shown in this table:

	R	error	L	error
Standard Cable	978 μΩ	± 3.0 μΩ	53 nH	± 0.4 nH
Low Z	972 μΩ	± 2.6 μΩ	806 pH	± 65 pH
Low Z Corrected	969 μΩ	± 2.6 μΩ	390 pH	± 3.8 pH

All the resistance values are within the 5% resistor tolerance.

Unlike lower value resistors, where the terminal resistance is negligible, the terminal resistance on this 1 mΩ part must be substantial. If the part were made from solid copper with the same dimensions, its end-to-end resistance would be about 50 μΩ, or 5% of the resistors value.

The resistance values from the fits may be low because a significant layer of solder built up on the resistor's terminals, which would lower the component's value, perhaps by as much as 10 - 20 μΩ. In addition, the resistor's manufacturer specified its value assuming a distributed contact onto printed circuit board pads. Our connection geometry is quite different.

Notice that the resistance value calculated from the corrected spectrum is lower than the uncorrected data by about 3 μΩ. This is close to the 4.5 μΩ resistance value calculated from the surrogate's spectrum.

We cannot be certain which resistance value is more accurate.

Correction for cable and fixture effects by subtracting a surrogate's spectrum assumes that the surrogate has zero resistance and inductance. If the surrogate has non-zero resistance or inductance, its subtraction can overcorrect the resistor spectrum.

Gamry Instruments' Accuracy Contour Plot defines two accuracy regions. The first is a region that can be measured with < 1% magnitude error and <2° phase error. The second is a region with < 10% magnitude error and < 10° phase error.

What is the highest frequency in our three resistor spectra that lies within these regions?

The limits are shown in this table:

	1% and 2°	10% and 10°
Standard cable	79 Hz	505 Hz
Low Z cable	5.0 kHz	31.6 kHz
Low Z corrected	12.6 kHz	63.14 kHz

The frequencies were calculated assuming the resistor's true value is fit value in that spectrum. The resistor is assumed to be perfectly non-inductive. The second assumption led to phase errors calculated as deviations from 0°.

In practice, the phase error limit was always exceeded at a lower frequency than the magnitude error limit.

Conclusions

In this Technical Note, Gamry Instruments presents a number of guidelines for accurate EIS measurements on low impedance cells. Galvanostatic cell control, a large AC current, and twisted-pair cell wiring are all important.

When these guidelines are followed, an EIS system equipped with a Gamry Instruments Reference 600 can accurately measure the impedance spectrum of a miniature, low inductance 1 mΩ resistor.

When the resistor spectrum is corrected by series subtraction of a low impedance copper surrogate, the accuracy of the measurement is extended to higher frequencies.

Assuming the 1 mΩ resistor that was used in this test is perfectly non-inductive, its impedance can be measured using a Reference 600 based EIS system out to 12.6 kHz.

Do the inductance values make sense? The inductance calculated from the resistor's spectrum was 806 pH. The inductance calculated from the surrogate's spectrum was 444 pH. The difference between these values (362 pH) is close to the 390 pH inductance calculated from the corrected spectrum.

Note that the inductance correction via surrogate subtraction did not involve subtracting one large value from another large value to obtain a small difference. If the resistor inductance and surrogate inductance were much larger than the difference between them, the value of the difference would be suspect. Cabling and fixtures would need to be very, very reproducible to allow this type of correction.

Some, or all, inductance remaining after spectrum subtraction may be real inductance in the resistor. Note that the 390 pH inductance value calculated from the corrected spectrum is slightly lower than the Vendor's claim that the WSL resistor has inductance between 0.5 nH and 5.0 nH.

In general, EIS measurements that involve inductances in the pH range are difficult and errors in the measurement can be large. Measurement of 1 mΩ at 1 MHz is virtually impossible.

Extension to Real World Devices

The miniature resistor used in this validation test is not intended to represent a typical ECS device.

Real world ECS devices are generally much larger than this resistor and one cannot easily solder to their terminals. However, the guidelines listed above are still useful.

EIS measurements on a packaged battery should always use a connection fixture to insure reproducible cabling. A battery surrogate can often be machined from copper or aluminum. The tinned wires on the Low Impedance cable can be soldered or mechanically connected to the fixture.

Fuel cells usually have fixed connection points for the current-carrying and sense leads. These are often bolts or screw terminals. The tinned wires on a Gamry Low Impedance cable can connect directly with these points.

Surrogate measurements on a fuel cell assembly can be made with metal foil in place of the fuel cell membrane(s). If you are careful to position your cell leads in a reproducible manner, the surrogate data and fuel cell data should have similar errors.

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734 Louis Drive • Warminster PA 18974 • Tel. 215 682 9330 Fax 215 682 9331 • www.gamry.com •info@gamry.com