

EIS of Difficult Samples



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EIS of Difficult Samples

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY(EIS)

Electrochemical Impedance Spectroscopy (EIS) is an incredibly useful technique that can be applied to a variety of systems. Many of those systems are straightforward and don't always special consideration during instrument setup. This white paper is designed to give you helpful information for systems that are a bit more challenging to measure. Typical examples would include: barrier coatings, very corrosion resistant materials, and very low impedance samples such as large supercapacitors (on the order of hundreds or thousands of Farads).

This document will provide useful information for how to get the best answer when performing EIS on your system. It will go through: what difficult samples are, the limits of the measurements, a refresher on instrumentation, what the EIS performance limits are, ways to make bad measurements, and then how to improve those.

What are difficult samples? For EIS, there are a few general categories of difficult samples; the primary categories are high impedance and low impedance. What these terms mean will differ from instrument-to-instrument and from system-to-system. For Gamry potentiostats, high impedance generally means giga-Ohms ($G\Omega$) and higher. Depending on exactly where you are in impedance magnitude, what system you're using, you might start to have issues when you get up into the high mega-Ohms ($M\Omega$) region, but for $G\Omega$ and higher, you are going to need some special considerations. Samples that have this level of high impedance are things like coatings, specialized materials, and very small [micro]electrodes.

On the other end, we have low impedance. When the impedance gets low enough, additional issues will need to be considered. For Gamry systems, we tend to mean less than one milliohm ($m\Omega$), though special considerations start to become necessary in general below 1 Ohm (Ω). The first consideration is simply whether to run potentiostatic or galvanostatic EIS. In terms of actual difficulty in making the measurement, for Gamry systems, that occurs starting with single-digit $m\Omega$ and below. At those low impedances the measurement becomes more challenging. Systems that are in the low end of the impedance range include batteries, electrochemical double layer [super]capacitors, fuel cells, and very large or porous electrodes.



There are other types of difficult samples to manage. Unstable samples are actually quite common—found in batteries, corrosion, biological systems, and more. Any time where the sample changes versus time, there exists the potential for instability, and instability leads to invalid EIS.

Further, there are other difficult samples to measure. If there are high temperature/high pressure considerations (e.g. in an autoclave), that can lead to grounding issues. There are other cases of grounded electrodes as well. Some samples are themselves more difficult to manage, things like curved surfaces. There can also exist issues related to reference path impedance or other setup challenges.

Some sources of limitations are discussed here. The cell cable itself is the first of these, because it is a physical object that can limit the upper and lower bounds of impedance, as well as both the real and practical upper frequency limit. It is possible to manipulate the cable configuration to improve those limits to a certain extent. For low current (high impedance) measurements, use of a Faraday cage is necessary to shield external noise sources. Moving to the hardware of the potentiostat itself, the lowest current range of a potentiostat puts a hard limit on its current measurement capabilities. High impedance means low current, so for some systems, the low current measurement capabilities can end up being limiting. This tends to be most relevant as the measurements approach the DC limit for impedance. For low impedance systems, it is low voltage measurement and/or control ability that becomes critical. For best low impedance measurements galvanostatic testing is required, so low voltage measurement capabilities are needed. Low noise potentiostats are going to have both better measurement of low, small voltages, as well as very low currents.

One specification that is not as commonly understood, but which is very important at the limit for EIS measurements is CMRR. CMRR stands for “common mode rejection ratio,” and a large value means that a system can better measure very small [voltage] signals even in the presence of a large [current] signal. Note that the inverse is also true, but since most potentiostats have more current ranges than voltage ranges, it tends to be more important for low impedance measurements than for high.

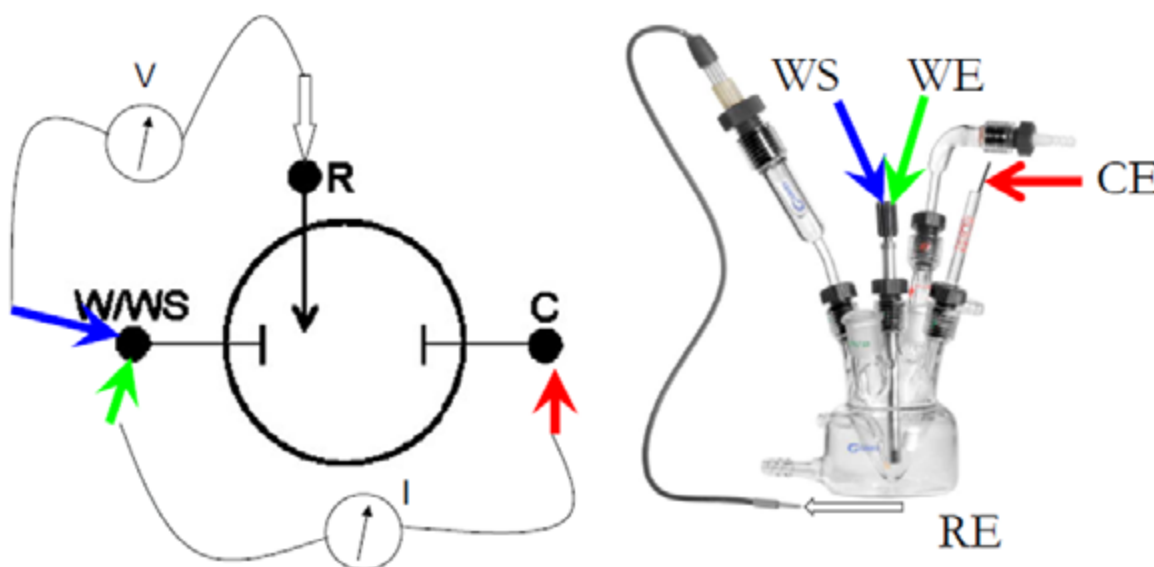
In addition to the hardware and cabling, there are also the reference electrode and reference path impedance which can limit measurements. On the cell side, reference electrodes are the single biggest source of limitations and problems. There can be other physical cell setup issues as well (positioning, distances, electrolyte...), and then there is the actual sample.

Looking at all these impedance limiting issues they can be broken down into limitations from the potentiostat itself and limitations that come from the cell side.

Note that the potentiostat itself constitutes more of those limiting factors above, but that does not mean it is the most likely limit in any given situation. It is, however, the one that produces most hard/absolute limits, and the part of the system where those limits can more easily and consistently be figured out. Because of that it is the hardware side that will receive the focus going forward, and so a brief introduction to electrochemical instrumentation follows.

A potentiostat is an instrument that measures and controls voltage between a working electrode and a reference electrode and that [usually] measures the current flowing between that working electrode and counter electrode. A galvanostat the inverse of that: it is a device that controls (and measures) current flow between the working and counter, while [usually] measuring the potential between the working and reference electrode. Modern electrochemical systems usually can work as both a potentiostat and a galvanostat. Additionally, they can work as a ZRA and an FRA. An FRA or frequency response analyzer is necessary for EIS, but it's the potentiostat/galvanostat side of that we really focus on, as most EIS limits come from there.

High performance potentiostats are always 4-terminal devices. Two of those terminals – named the reference and work sense leads – are sense terminals, which measure voltage. The other two terminals – named the counter and working leads – are the force terminals, which carry the cell current.



Note that potential is only measured through 1/2 of the cell.

Figure 1: Standard 3-electrode cell setup shown schematically (left) and actual cell setup image (right)

For most electrochemical experiments the 4 leads are connected to three electrodes in the working cell. As shown in Figure 1, the working electrode receives connections from both the current (working, force, green) and the sensing (work sense, sense, blue) lead. The second sense lead (reference, white) is connected to a reference electrode, and the second current carrying lead (counter, red) is connected to a counter or auxiliary electrode. Note that this configuration only measures the potential difference from the working electrode to the reference electrode point. The only impedance that is being measured is that of the working electrode and some of the solution/electrolyte resistance.

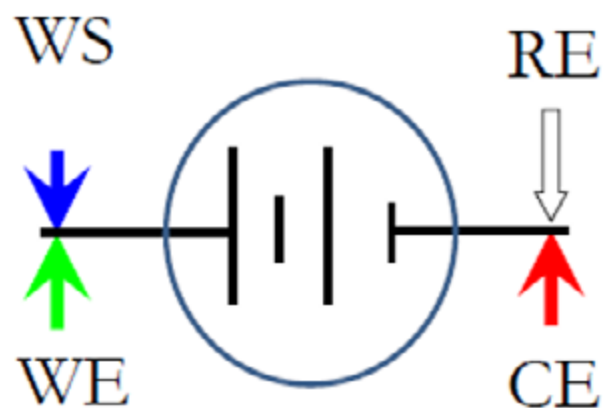
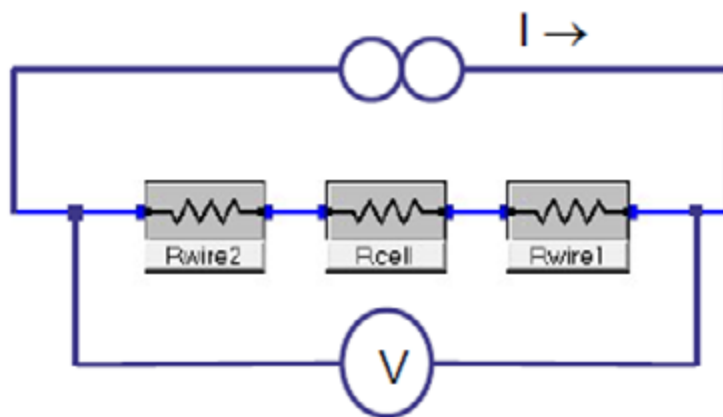


Figure 2: A two-electrode setup one force (current) and sense (voltage) lead on each electrode/terminal.

The above setup describes the three-electrode four-terminal experiment, and that is the most common electrochemical cell setup, but for EIS measurement, 3-electrodes are not always possible or desirable. There can be reasons that a third electrode (reference electrode) may not work. Most often this is when the cell under test is packaged as two-electrode, two-terminal device, like batteries and fuel cells as shown in Figure 2. In these cases, instead of having the reference (sense) lead going to an independent reference electrode, it is connected to the same terminal as the counter electrode. This type of configuration can also be used for troubleshooting: by switching from three-electrode to two-electrode we eliminate the reference electrode as a source of potential problems and also measure the voltage of the counter to see if there are any issues with the current path. Note that for a 2-electrode configuration the measured system impedance is more complicated, but the full system is being measured which can isolate where problems may be occurring.

2-Terminal

These connections measure both the cell impedance and the wire resistance



4-Terminal

These connections measure only the cell impedance

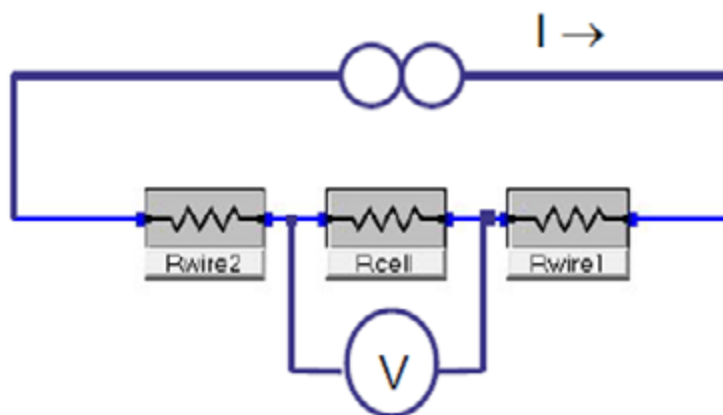


Figure 3: Schematic for 2 terminal and 4 terminal connections to a 2 electrode system.

Note also that a 2-electrode measurement can be made in either a 2-terminal or a 4-terminal mode as shown in Figure 3. Simply: for a 2 terminal setup the force and sense leads share a contact point, whereas for a 4-terminal setup the force and sense leads make separate contacts to the electrode/terminal. A 4-terminal setup will not be measuring the contact resistance of the force leads and so gives impedance for the cell only. In practice this matters more for lower impedance systems. To clarify: two-electrode means that there are two electrodes in the cell/system. A two-terminal setup would mean the sense and force leads have been shorted together before connection to the cell electrodes/terminals. It is possible to make a 4-terminal connection to a 2-terminal device.

Total EIS system performance

Some of the limitations that difficult samples can run up against are the limits of the instrument being used to make the measurements. Because of that it is a good idea to understand what those limitations are. Because every system and setup environment is going to be slightly different, they will be discussed here in somewhat idealized terms. In practice it is a good idea for a researcher to test things out and see what the actual system limit is for a given setup.

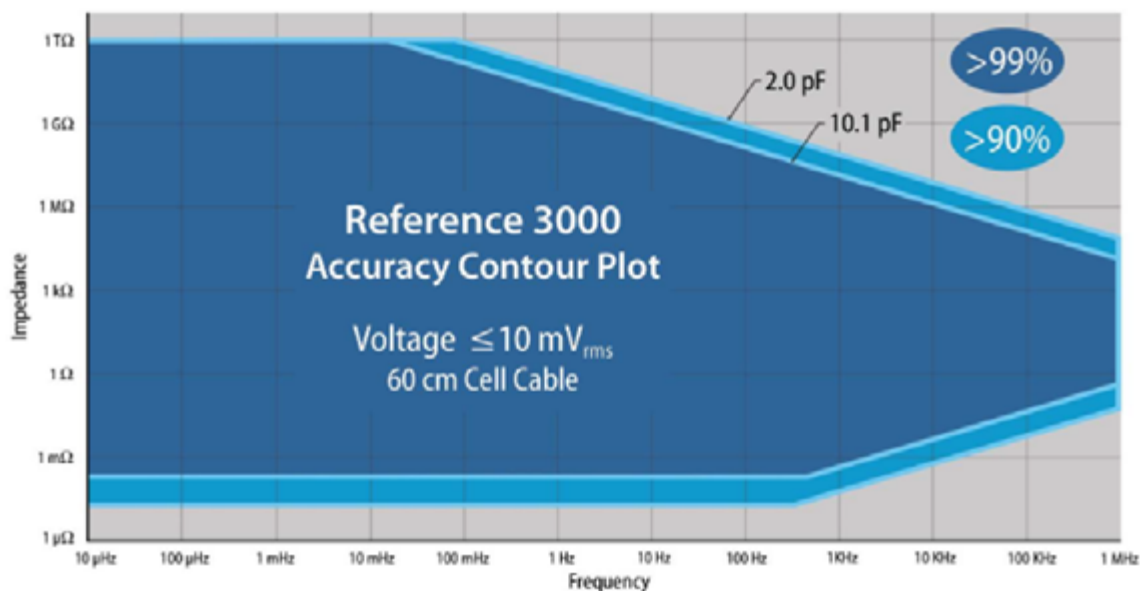


Figure 4: Accuracy Contour Plot for a Gamry Reference 3000 potentiostat.

One of those ways to see a system's limits is an accuracy contour plot (ACP), shown in Figure 4. This can be found for most EIS-capable potentiostats. Unfortunately ACPs are not all determined in the same fashion, so it isn't necessarily possible to directly compare them. Attention must be paid to both the accuracy contour map and how it was made. For Gamry systems, the ACP is generated using the standard cell cable as well as realistic and typical operating parameters for EIS. That would mean an RMS AC voltage of ten millivolts or less, potentiostatic control for the high impedance side, and galvanostatic control for the low impedance side.

When looking at the ACP, the accurate impedance bandwidth changes with increasing frequency. The actual frequency limits are dictated by the hardware itself. At lower frequencies within that range the impedance accuracy limits are dictated by hardware limitations, whereas at high frequency the limits tend to come from cabling effects.

The low frequency, high impedance limit has to do with the lowest current that the system can accurately measure, which couples the minimum current range with things like system noise limitations. At the absolute high impedance, low(er) frequency limit is the printed circuit board resistance itself, which puts a limit on what any PCB based system can do—note that the teraohm level is approaching this PCB limit.

For low(er) frequency, low impedance measurements, the limitation is related to the common mode rejection ratio (CMRR). The CMRR relates to a instrument's ability to measure a very small signal in the presence of a paired large signal. For low Z measurements a high current signal is used to force a voltage response into a measurable range, some of that signal from that current can bleed over into the voltage measurement circuitry and that ends up limiting the impedance measurement on the low side.

As mentioned above, limits at higher frequencies tend to come from the cabling being used. The cell cable has capacitance, which puts an upper limit on impedance measuring and an inductance that puts a lower limit on the measurement capabilities. Note that those can be compensated for using cable corrections, but they are still present and signal traveling though the cell cable also travels through these elements. If the cell cable is not part of the ACP then the accuracy noted is not correct at higher frequencies. Further, different cell cables are going to give you different limits, with longer cell cables having narrower accuracy windows.

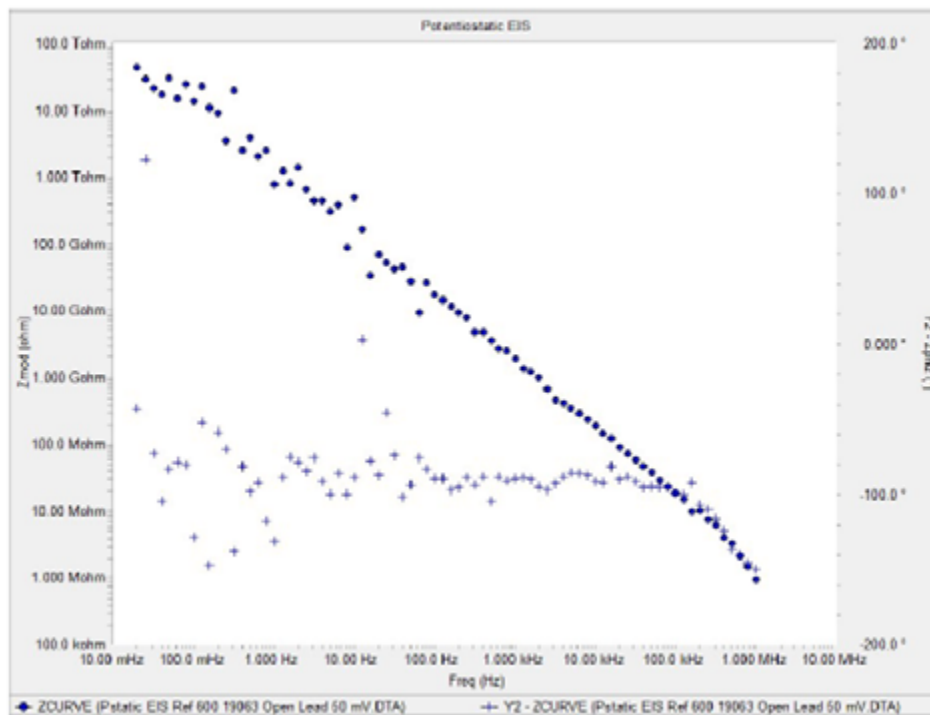


Figure 5: Open lead curve

The ACP shown in Figure 4 was made by measuring precision resistors under approaching ideal conditions. Conditions will not always be the same, so it is good practice to do a quick accuracy test for a given system and setup. An open lead curve (Figure 5) approximates the absolute high impedance limit for a system—note this is not the same value as the ACP limit, as it would be approaching 0% accuracy. This test must be done in using two Faraday cages. Complete details for how to measure an open lead curve, as well as other quick check can be found on the Gamry website, but a brief description follows.

To measure open lead, the working and working sense leads are shorted together and placed inside of a Faraday cage. The counter and reference leads are also shorted together and either left outside of the Faraday cage or, ideally, placed in a different Faraday cage. Run a potentiostatic EIS experiment with 50 mV AC signal and a DC of 0 vs. Eref. The resulting EIS spectrum should appear as that of a capacitor: roughly negative ninety degrees phase shift, and a straight line of increasing impedance from high to low frequencies. At very low frequencies it may start to flatten out. Systems with poor low current measurement capability will flatten out at lower impedance values. This is not seen in Figure 5 because it was not run to a low enough frequency for that to occur.

For low impedance measurements, like energy storage and conversion devices, the equivalent series resistance (ESR also called high frequency resistance or HFR) causes efficiency loss, and is one of the more important figures of merit to get from an EIS spectrum. Low impedance devices are generally tested galvanostatically instead of potentiostatically, because even a small AC potential across a mΩ or Ωμ level impedance can produce currents too large for the system to handle, and reducing the potential to the point where the current is manageable is often not possible—it is easier to measure μV AC than it is to control μV AC.

Without prior knowledge it is difficult to determine whether potentiostatic or galvanostatic is the correct choice. In those cases, potentiostatic is the “safer” choice, as small voltage perturbations producing high currents are less damaging to a cell than small current perturbations producing high voltages.

Hybrid EIS is a mode which helps to deal with systems that transition from very low to intermediate impedances. It utilizes galvanostatic control but adjusts the signal magnitude at lower frequencies to prevent overpolarization of the cell and maintain a linear response.

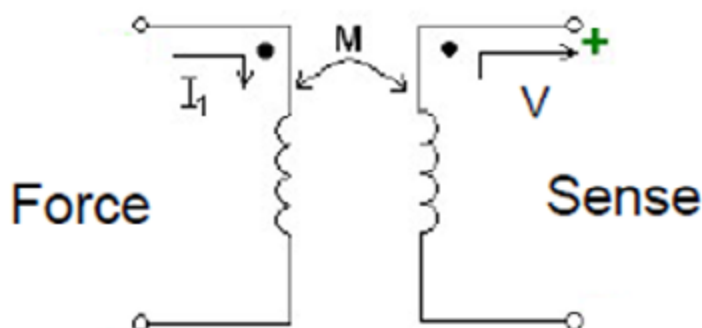


Figure 6: Mutual inductance

Since ESR measurements occur at higher frequencies, the mutual inductance from the cell cable is often a complication in getting accurate results. As noted in the accuracy contour plot discussion, this is a limitation for high frequency, low impedance measurements. Mutual inductance is primarily due to the cell cable—current carrying and voltage measuring lines running alongside each other—and results in an inductor in series with the electrochemical cell under test. Longer cell cables are worse than shorter ones, and single bound cables are worse than cables with sense and force leads separated. There are ways to reduce this effect based on setup.

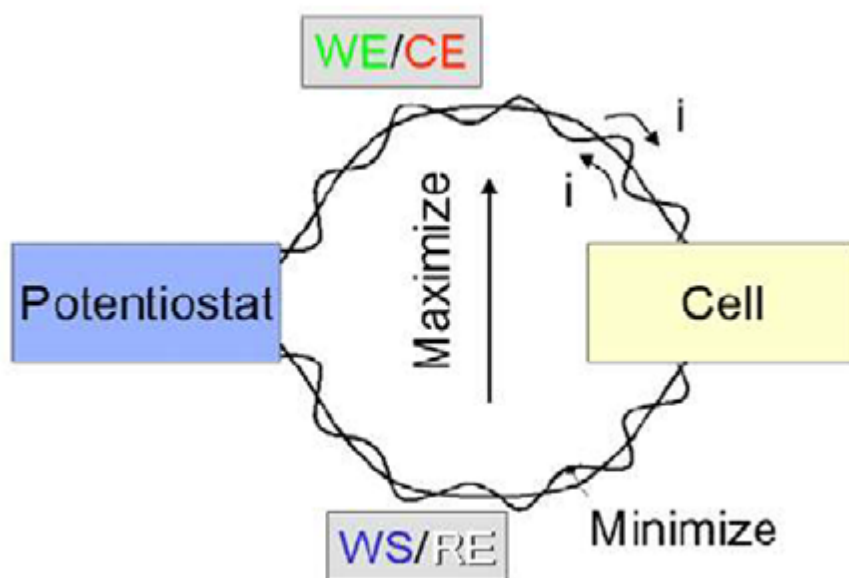


Figure 7: Cell cable setup to minimize inductance.

When measuring low current devices, it is very important how you connect your cell. Ideal configuration involves pairing the force leads together—working and counter electrode leads—and pairing the sense leads together—working sense and reference. Then make twisted pairs of the two lead pairs—by twisting them, that electromagnetic field is reduced and minimizes the amount of pickup. Finally, to the extent possible, separate the force leads from the sense leads. This setup will minimize the inductance due to the cell cable.

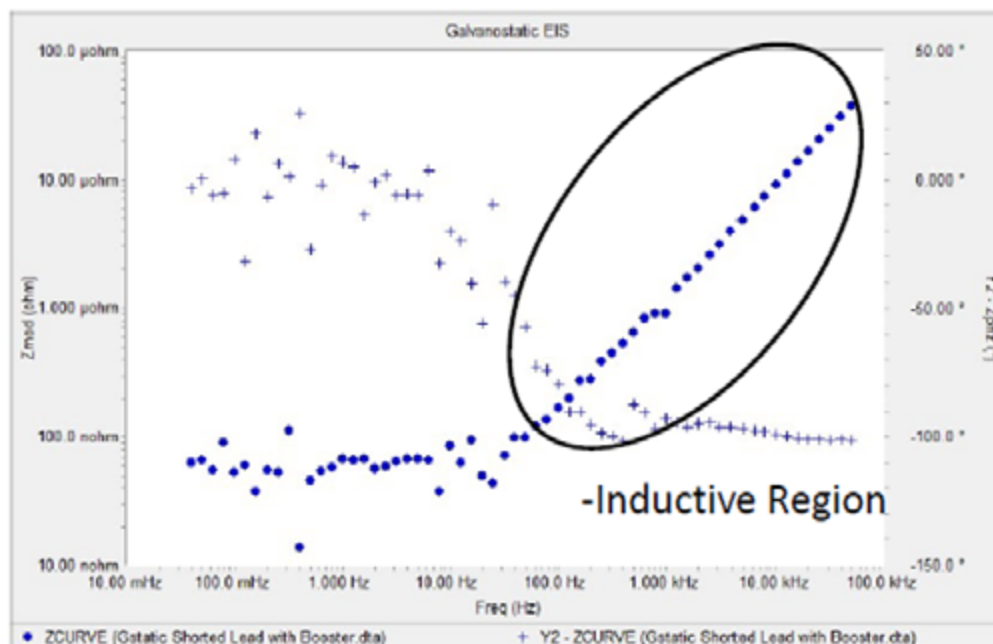


Figure 8: *shorted lead curve.*

To test the instrumentation limit for low impedance tests, a shorted lead experiment can be performed. To generate a shorted lead curve, all the leads should be shorted together. The result should have two features. One is that mutual inductance, with the setup as described above to minimize its effect. The other element is at lower frequencies. Once the inductive region rolls off at lower frequencies, the limitation is resistive and at these frequencies it is the CMRR that limits the measurement. In Figure 8, the CMRR limit corresponds to about sixty-seven nanoOhms (Ω).

Please note that when shorting leads together, care should be taken to avoid contact resistance pickup and to be measuring with a shorting material that will have less impedance than the system limit. Copper braid can be used for a quick test, but copper braid impedance is about ten Ω per millimeter, and a high performing system will be able to accurately measure that impedance. For the shorted lead shown above, a pin was connected to a brass block. Force leads were connected on one side of the block and both sense leads were connected to the pin to minimize any real impedance of the shorted lead test fixture.

Now that system limitations have been addressed, it is possible to discuss other aspects of making difficult measurements—both good and bad. There are a lot of ways to make bad measurements, but some ways of making bad measurements do happen more often than others.

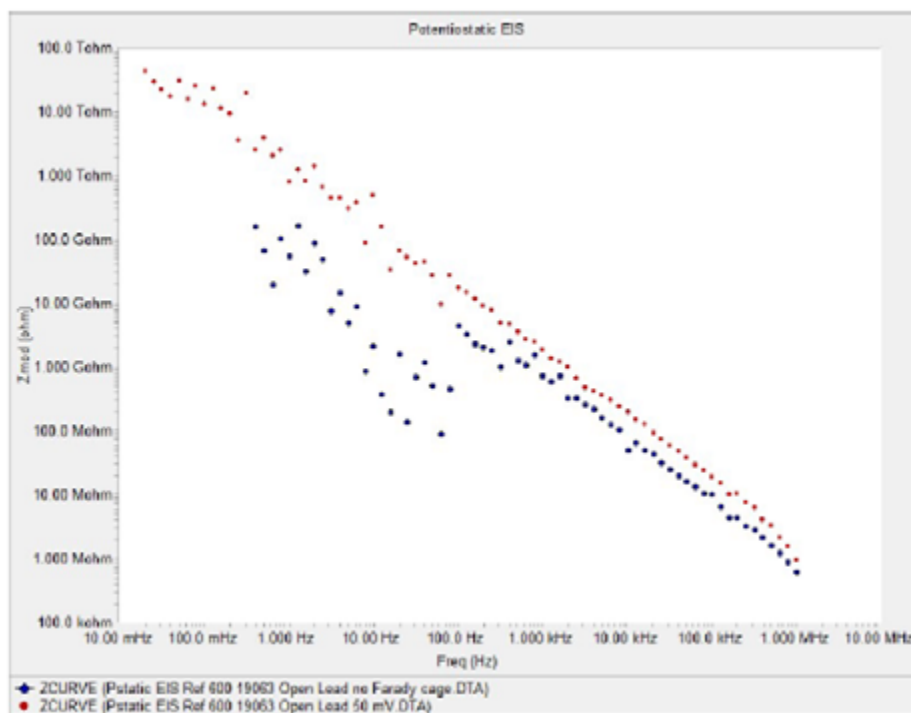


Figure 9: *Good and bad open lead tests*

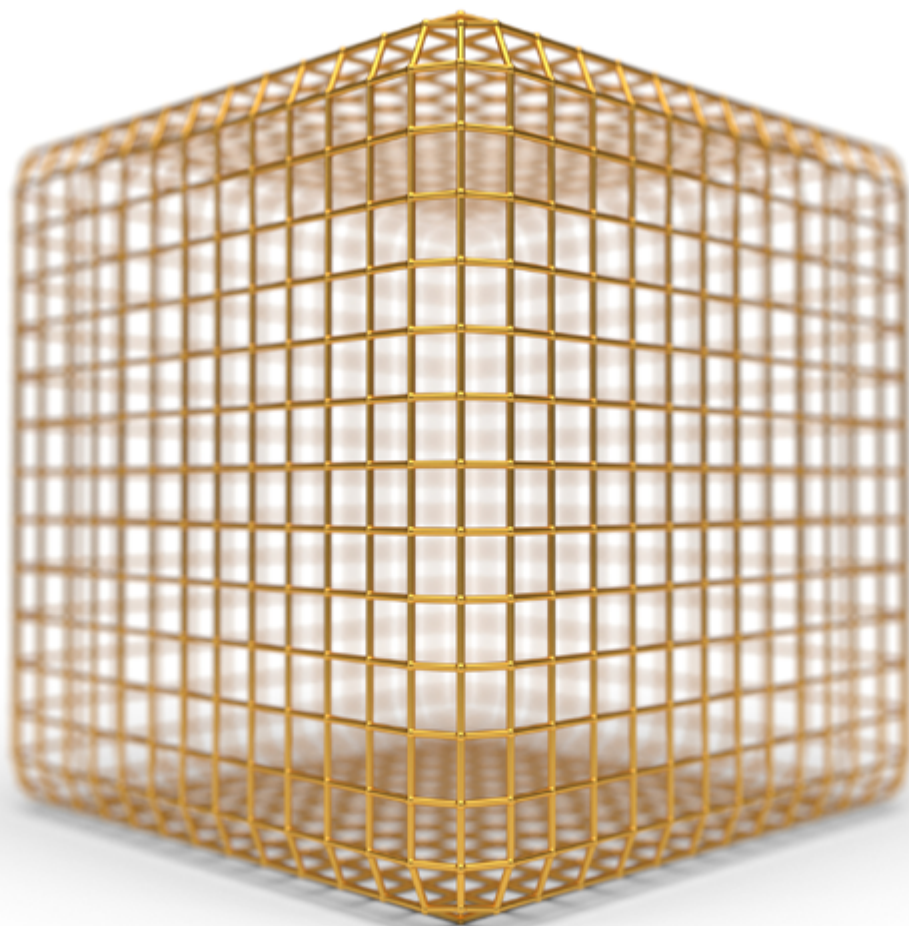
When making low current, high impedance measurements, it is important to use a Faraday cage. Figure 9 shows the open lead curve from with a Faraday cage (in red), and without the Faraday cage (in blue). There are two changes that can be noted. First is a slight but significant change in the capacitance. The second, more dramatic difference, is a large shift and increase in the noise when at lower frequencies.

The entire spectrum is worse in the absence of a Faraday cage. As a general guide, if impedance is $>100\text{ M}\Omega$, or current $<1\text{ }\mu\text{A}$ the measurement should be made inside of a Faraday cage. Some environments may be particularly noisy—e.g. if there are pumps or other unshielded electronic systems nearby—and in those cases a Faraday cage may be required even at higher currents and lower impedances. Because it is an environmental effect, it is possible that the limits where a Faraday cage becomes necessary will differ from lab to lab.

Another common issue when making measurements is system grounding. All Gamry potentiostats are electrically isolated from earth ground (commonly called floating). This isolation is a requirement if you have experiments with grounded electrodes, if you're running electrochemistry inside of an autoclave, or if you have multiple electrodes and systems connected into the same cell. An example of that last case would be a bipotentiostatic experiment, where two working electrodes, are being measured and controlled against shared reference and counter electrodes. For some energy tests, like fuel cells, the terminals of the system are connected to an electronic load that handles the high DC current being produced by the cell, and then the potentiostat is connected in parallel with that to provide a small AC signal on top of the DC signal. Because the electronic load is earth grounded, the entire system is earth grounded. Earth grounding is the default assumption for most pieces of equipment that are plugged into the mains, so any time there are additional voltage leads connected for sensing or for different types of control or measurement within the cell, a floating potentiostat may be necessary.

The Gamry cell cables have a black lead. That black lead is a float ground, because even though the system is isolated from earth ground, it still has an internal “ground” reference against which voltages are measured. When using a Faraday cage, the ground reference of the potentiostat must be connected to the Faraday cage. If the ground lead is not connected then the Faraday cage can actually make measurements worse because the Faraday cage then acts as an antenna and introduces noise into the cell.

A floating potentiostat can be earth grounded. Earth grounding can help reduce noise: if you have very low current signals, very high impedance, and you do not require the floating performance of the potentiostat, you can earth ground the system to help reduce the noise. If you want to earth ground a system, it is important to only use one point of ground for earth. There is a ground lug on the back of most Gamry systems, that is usually the recommended grounding point. If the potentiostat is connected to earth and a Faraday cage is being used, then the Faraday cage should not have another ground connection. If, however, the Faraday cage is already earth grounded, then connecting the float ground lead of the potentiostat to that Faraday cage will also earth ground the system and the ground lug on the back should remain disconnected. If there are multiple contacts to earth ground, it can create a ground loop which can increase the noise of the system instead of lowering it.



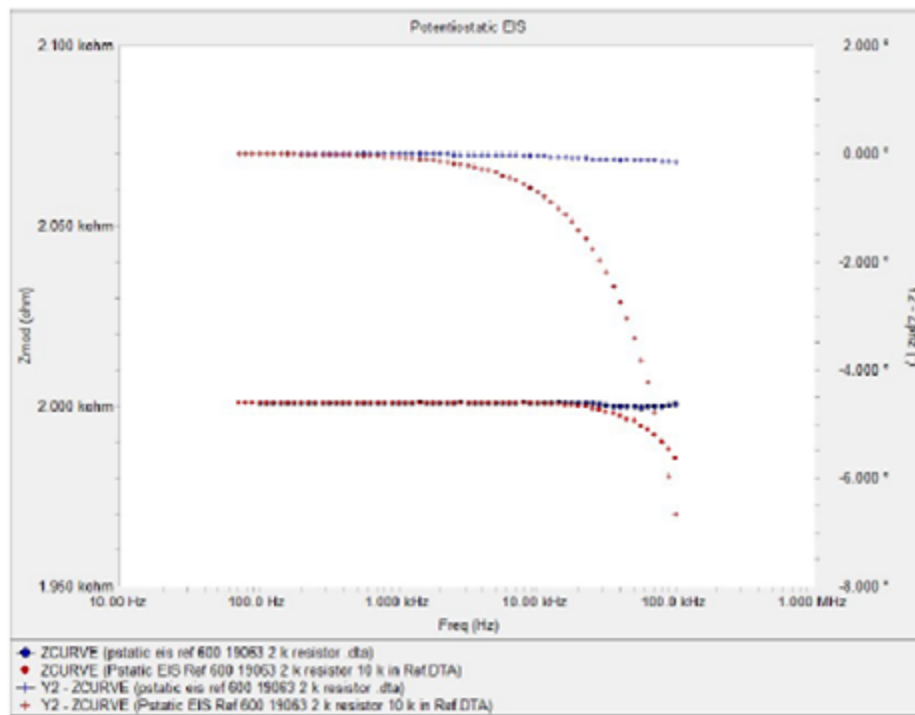


Figure 10: EIS measurement without (blue) and with (red) excess reference path impedance

High impedance reference electrodes are still another common cause for making bad measurements. In a typical 3 electrode cell, there is a reference electrode. We don't measure the impedance of the reference electrode but it is possible the impedance of the reference electrode can have an impact on the device performance in the system that you're measuring. Figure 10 shows two EIS spectra that were recorded on a simple two k Ω resistor measured up to 100 kHz. The blue spectrum is what is expected: 2000 Ω impedance and 0° phase shift across the entire spectrum. For the red spectrum, an additional 10 k Ω was connected between the reference lead and the dummy cell. The current did not flow through this resistor and so it is not part of the impedance spectrum, which remained 2000 Ω . Despite it not being measured, it is still impacting the spectrum by slowing down the measured voltage response through the reference lead. The effect shows up with higher frequencies, first as a deviation on the phase measurement, and at higher frequencies on the modulus. So high impedance on the reference electrode, even though that impedance is not directly measured in a three-electrode cell, can still affect the resulting spectrum by slowing down the voltage measurement. If this reference electrode impedance gets too high, then the system can start to oscillate under feedback control, but even at lower impedance it can still affect the EIS performance. The most likely cause for a high-reference electrode impedance is a bad isolation frit. For a slower DC measurement, like polarization resistance, there is less sensitivity than high speed, high frequency measurements like EIS. When reference impedance is 2-3 times higher than used in the Figure 10 example, even slow measurements would start to be problematic, or not possible.

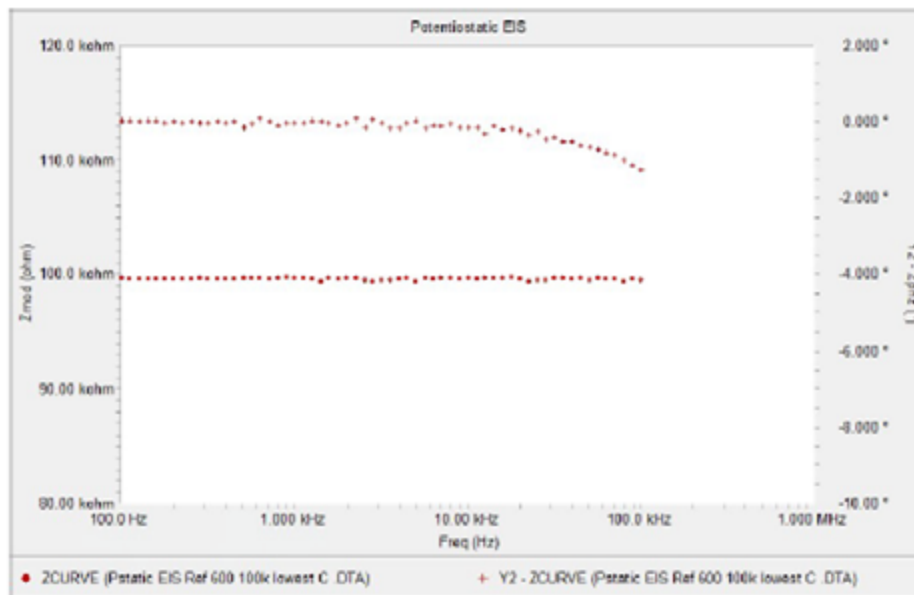


Figure 11: EIS of a 100 kΩ resistor with cable connections designed for high Z measurements High impedance reference electrodes

Sticking with issues that cause issues for high impedance measurements, another problem that can arise is the stray capacitance from the cell cable and leads/connections. This is primarily an issue for coatings, where the coating capacitance itself may be the same order of magnitude as the cable capacitance, but it can become an issue with any system that has high impedance and small capacitance and there are a few different ways to deal with this. Figure 11 shows an EIS spectrum of a 100 kΩ resistor with the leads/connections made to minimize cable/connection capacitance pickup. To do that, first the respective sense and force leads are paired: working with working sense on one side and counter with reference on the other. Then those pairings are separated from each other as much as possible, and when the connections were made to the resistor, the alligator clips were pointed towards each other. The resulting EIS spectrum shows good phase and modulus response, with only a small deflection on the phase at higher frequencies.



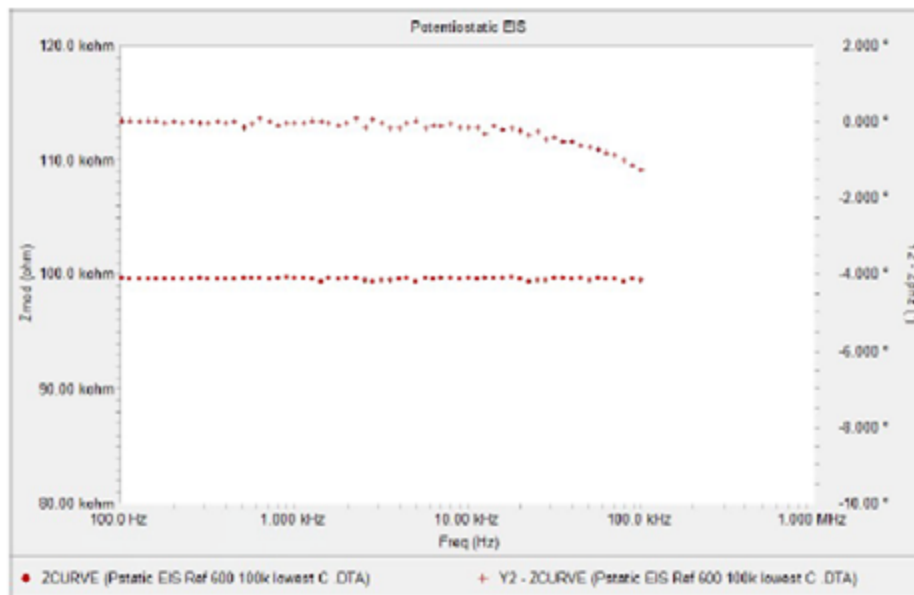


Figure 12: EIS of a 100 kΩ resistor with cable connections designed for low Z measurements

Making another measure of that 100 kΩ resistor, but now with the same four-terminal connections that would be used for a low impedance device as discussed earlier produces the spectrum seen in Figure 12. The phase deflection has increased from under 2° to 10°, and the modulus has also deflected down from the 100 kΩ value. It is possible to connect the leads in such a way to make this spectrum deflect even further, by lining all the leads up and bringing them in in parallel. The terminations for these cables, alligator clips, are unshielded metal as are the banana jacks underneath. Because there is no shielding they are going to have potentially higher capacitance than the shielded cable running up to the termination (note that even with shielding, there is additional capacitive pickup from the cables as well). For high impedance measurements, therefore, it is best to try and minimize the capacitance of the cell cables and terminations. That said, ideal connections are not always possible, so in those cases, it is good to understand that there may be some effect on the measurement due to cabling setup.

It is possible to make poor connections for low impedance systems as well. Figure 13 shows the results from three different connections setups to a 5 F capacitor. The worst of the group connects as a two-terminal device by having the sense leads and force leads shorted together before they make contact with the terminal. Additionally, the cabling was all run in together, mostly in parallel. It is possible to do a little better by pairing the sense leads together and the force leads together and making twisted pairs with them. That setup helps reduce the inductance but is still making a two-terminal connection. The best way to make this measurement is, again to have the sense leads and the force leads as twisted pairs, but also to separate those pairs from each other as much as possible, and to have distinct connections to the terminals making a 4-terminal contact. That “best” setup makes a large difference by eliminating the contact resistance as well as minimizing the inductance.



Figure 13: EIS measurement of a 5 F capacitor with 3 different connection schemes.

Quick note: the ideal cable setup up for a low impedance system is bad for a high impedance system and vice versa. In general, what you want to think about when you're doing this: for a high impedance setup, minimize the capacitive pickup. For low impedance, minimize mutual inductance. The twisted pair does improve low Z measurements, but not high Z. As most researchers will only be doing either high or low impedance measurements, cabling is not as likely to end up in the wrong configuration once setup correctly.

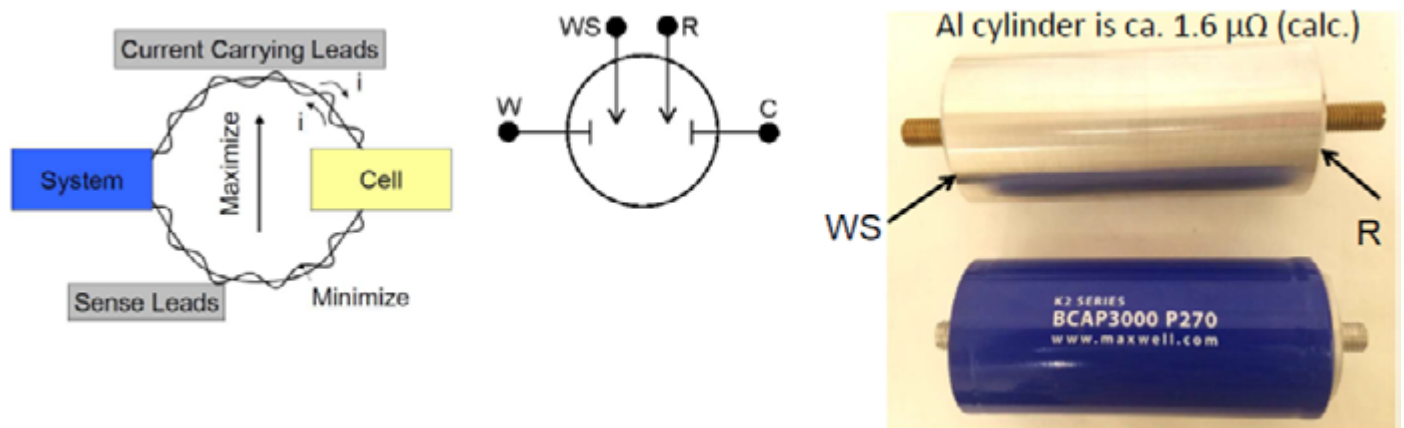


Figure 14: Connection schematics for and image of a 3000 F capacitor and its low Z surrogate.

At the extreme low Z end, not just mΩ but down to the $\mu\Omega$ range, another tool may become useful: a low impedance surrogate or dummy cell. A low Z dummy cell or surrogate should be designed to have the same setup up geometry as the actual cell to be tested, but with much lower expected impedance. Note that the surrogate doesn't have to be exactly the same size and shape, though that might be helpful if there's other types of environmental effects to be addressed, like setup effects.

The rightmost image in Figure 14 shows a surrogate for a 3000 F capacitor made of a solid aluminum cylinder with brass threaded rods at the terminals. It is important to note that these brass threads to that aluminum are going to have a contact resistance which is measurable. To mitigate that—as was done when the measurements shown in Figure 15 were made—the sense leads were in contact only with the aluminum, so the current transition from the brass into the aluminum was not sensed, though the whole of the aluminum bar was. The current carrying leads were connected to the brass but since the voltage is not measured there the contact resistance for the current carrying leads is not part of the spectra generated. The calculated impedance of the aluminum block is about $1.6\ \mu\Omega$.

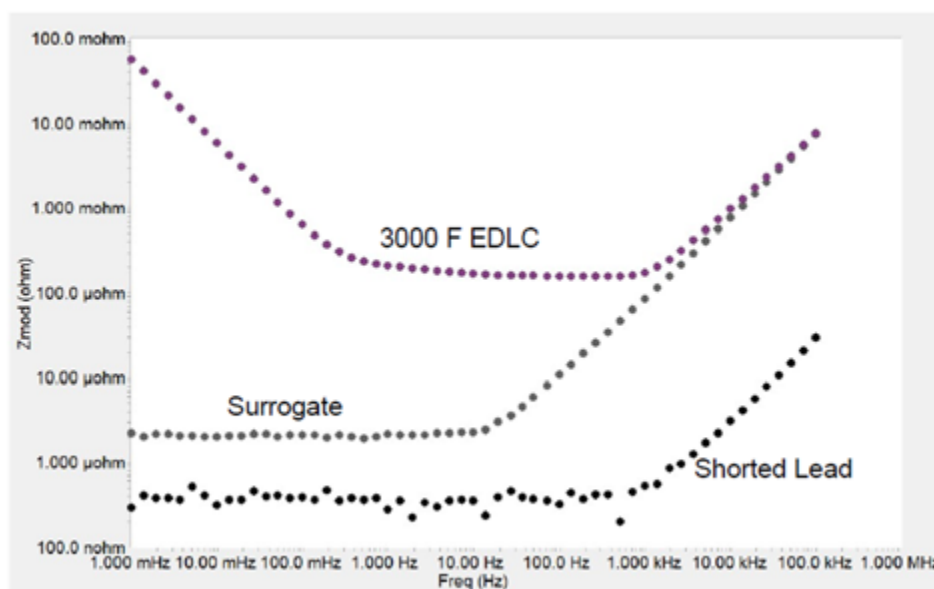


Figure 15: EIS spectra for a 3000 F EDLC, its surrogate, and a shorted lead (Bode plot of modulus).

Looking at the spectra from the 3000F capacitor, surrogate and a shorted lead test in Figure 15 shows how a surrogate can be useful for a real cell test. Note that the shorted lead test here was not as ideal a setup as the one earlier as it shows about $300\ \text{n}\Omega$ instead of $60\ \text{n}\Omega$, but the point here is actually to look at the inductance. The idea behind using a low Z surrogate is to have the same connections and cable placement as will be used for the actual cell test which means the inductance measured for a surrogate will be the background inductance for the actual cell test. The shorted lead, because it is not mimicking the cable placement/connections of the cell test, tends to have a much lower inductance. In Figure 15 the inductance from the surrogate is very similar to that of the capacitor by itself. What that means is that almost all of the inductance in the capacitor measurement, even though it's much more than the shorted lead, is actually due to the setup and configuration and not the capacitor itself.

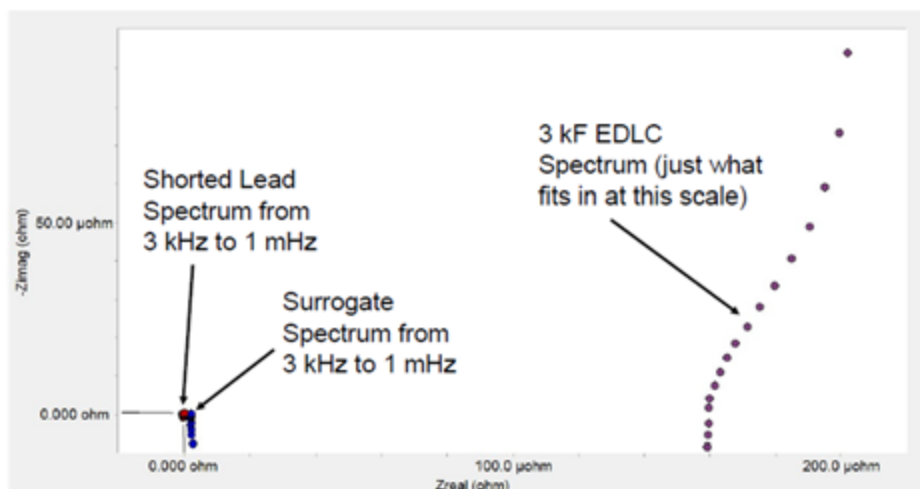


Figure 16: EIS spectra for a 3000 F EDLC, its surrogate, and a shorted lead (Nyquist plot).

The image in Figure 16 is the same data from Figure 15 but shown as the Nyquist plot. Energy device impedances are often shown in Nyquist form, but as can be seen here, some features are not as obvious in this format. In particular, the surrogate looks more like the shorted lead on the Nyquist, and the inductance cannot be as easily compared.

Quick note regarding the results shown in Figures 15 and 16: the high-performance system that was used to make those measurements is the best one for making low impedance measurement. Using that system to test the 3000 F capacitor, but deliberately connecting it poorly (i.e. the “bad” test from figure 13) gave an ESR of $\sim 250 \mu\Omega$; switching to four-terminal dropped the measured ESR down to about $165 \mu\Omega$, and the “best” setup, gave an ESR of $\sim 150 \mu\Omega$, so $150 \mu\Omega$ is roughly the ESR for this capacitor with the capacitance of 2700 farads. Note that the specified values for this capacitor are an ESR of $290 \mu\Omega$ and 3000 F. When it comes to AC (EIS) versus DC testing: the specified ESR value is probably less accurate than the measured one. The specified capacitance, however, is more accurate than the measured value from the EIS spectrum above. The reason is the AC capacitance measurement is the double layer capacitance only. EDLCs tend to have pseudo-capacitive effects that do not show up in most EIS spectra. They may become apparent at extremely low frequencies, but generally it is easier to actually get a good value using a DC test like galvanostatic charge/discharge.

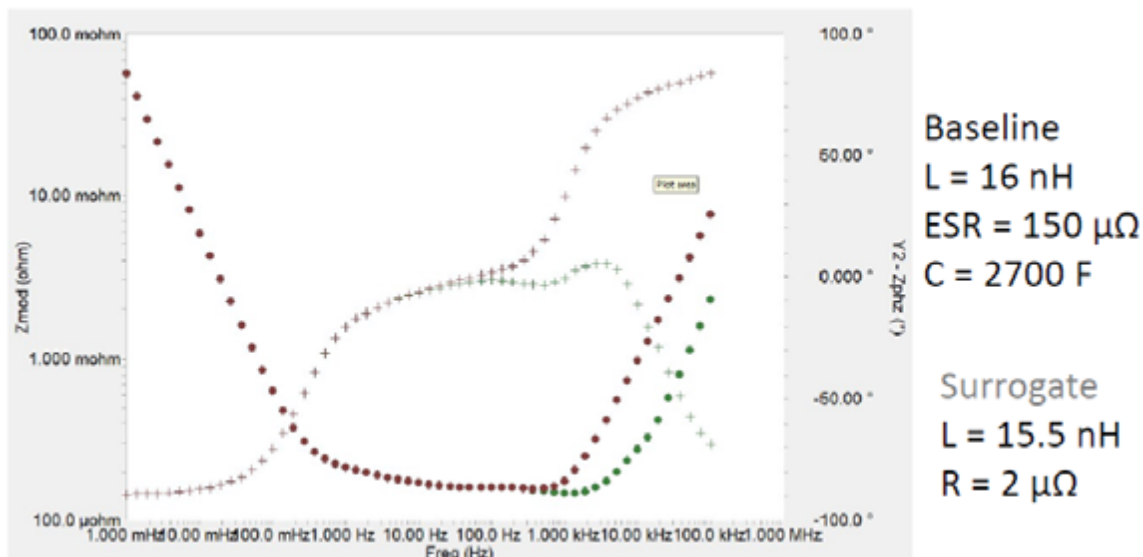
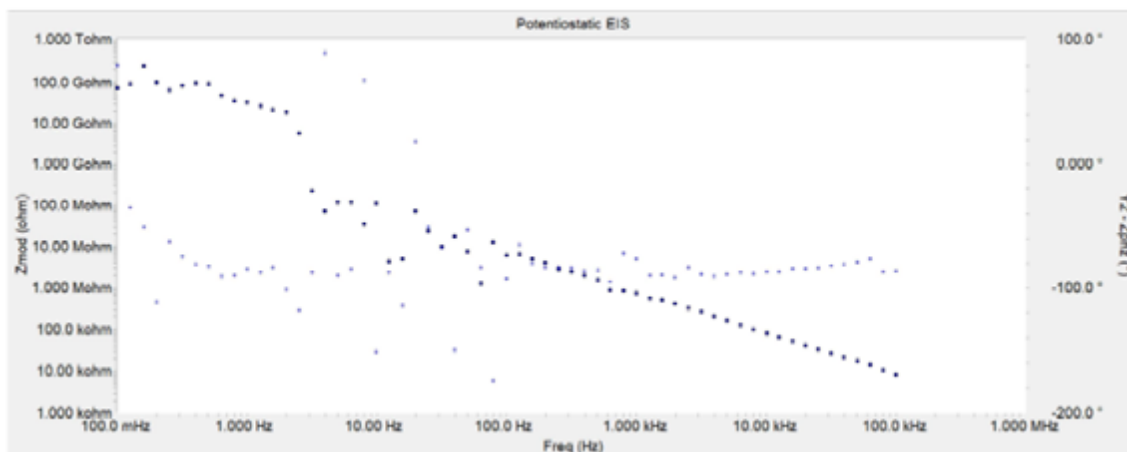


Figure 17: background subtraction

In addition to inductance comparison another thing that may be possible when using a surrogate is to do background subtraction. Background subtraction for EIS can improve values, but it must be used carefully. The surrogate provided an inductance and a series resistance, but only the inductance can be subtracted from the actual cell system. Figure 17 shows this, and particularly shows one of the pitfalls of doing background subtraction. The base spectrum gave 16 nH, and 150 $\mu\Omega$. The surrogate had a slightly lower 15.5 nH which can be subtracted. The result still looks inductive, but an examination of the phase, shows it going the wrong direction. There are a couple reasons for this behavior. First, whenever subtracting anything where the result approaches zero, the result is likely to be dominated by noise and artifacts. The second possible issue is that when doing background subtraction the subtracted element needs to be true to what is actually present. The mutual inductance that shows up at high frequencies is not an ideal inductor. A better representation would actually be a constant phase element, with the phase allowed to go positive (inductive). If the wrong element is subtracted out, again, it induces artifacts. Subtraction tends to work a lot better for measurements where there is a known value. A good example of that is: if one has a full cell and a three-electrode cell, then both the full cell and the three-electrode cell can be measured, then the three-electrode measurement could be subtracted from the full cell measurement to get the impedance on the second electrode. That works fairly well. It can still be problematic when approaching instrumentation limits, but it may also be the best way to get a better value near those limits.



Sample is Al in "electrolyte"

Figure 18: Poor EIS spectrum of aluminum.

Difficult measurements are not limited to those that take place near the system limits and/or due to poor physical (cable) setup. Some measurements are difficult because of samples themselves. One issue that arises across a broad range of electrochemical systems, is stability. Figure 18 shows an EIS spectrum of aluminum in some unknown electrolyte. For those who are not familiar with aluminum: the metal, in the presence of oxygen, will have an aluminum oxide film on the surface. This oxide film serves to protect the underlying Al from further oxidation, and a good quality oxide layer, in a non-aggressive electrolyte, will have an EIS response that is capacitive. The aluminum oxide is the dielectric material and the electrolyte on one side of that and the aluminum on the other serve as the conductive plates. This capacitance is like a double layer capacitance but tends to be much smaller since it is the thicker oxide film that serves as the dielectric, not the very thin layer of solvent between a bare metal and ionic species in solution.

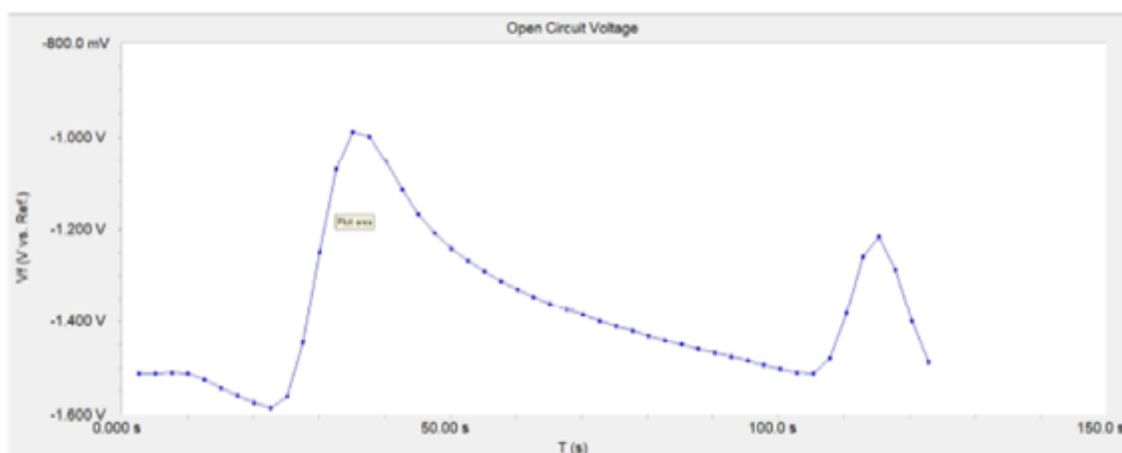


Figure 19: Open circuit potential of the sample with EIS spectrum shown in Figure 18.

The EIS spectrum in Figure 18 is not good, and the reason for this is because the electrolyte in that case contained chloride. Chloride is a common pitting agent for metals in general, and for aluminum in particular. Because of the pitting that occurs in the presence of Cl^- , the sample impedance is not stable—an opening pit will have lower impedance and when it closes the impedance goes up again. Figure 19 shows the open circuit potential from that same experiment. At the beginning it seemed rather stable, but then it shifted. After that the sample seemed to be restabilizing; then it shifted again. These are likely pitting events, and they doesn't always look as nice and dramatic as these do. Sometimes the data simply look noisy or somehow ugly. The exact appearance depends on several factors including how quickly pits are initiating, how long they stay active and the extent and speed with which they passivate.

Stability is not just an issue for aluminum and other passivating metals. It can be many varied electrochemical systems. Batteries are another. For example: when trying to run EIS on a primary cell, the problem is a primary cell doesn't recharge, so a small DC offset current is required so that the absolute current never reverses to the charging direction. This means the cell is constantly discharging during the experiment. If the impedance measurement takes too long, it could finish at a significantly different state of charge and therefore voltage than it started at. That can mean invalid EIS data. Background correction can account for some of the drift, but if the change was sufficient it is possible that there are effectively two different systems: one at the start and another by the finish, and so the entire spectrum will not be of the same system. Biological systems—that could be an in vivo or in vitro experiment, or testing using real water samples like from rivers or the ocean, where biological molecules and organisms can come into contact with the electrode—also affect system stability. Biofouling changes the performance, changes the impedance, and changes the stability of an electrochemical system. If the systems at the beginning and at the end of the experiment are not the same, the EIS data are harder to interpret. So what types of fixes are available?

Well, if possible, change the cell setup and electrolyte to something that will be more stable. Since that is often not possible there are other things to try. One is to use a smaller area. A smaller area is sometimes helpful because a smaller area electrode is going to be faster-responding which means the low frequency information is available at higher absolute frequencies than it would be with a larger electrode. This doesn't work for all stability issues, of course: a small electrode area for something like pitting may have a much more dramatic effect when that pitting initiates as a pit will represent a larger fraction of the total area. Still, when it can be used, a smaller area speeds things up and allows for shorter total times for EIS measurements. There are other ways, aside from using a smaller electrode, to speed up the experiment. When running Gamry EIS experiments, the setup window includes checkboxes noting “fast” “low noise” and “normal” which can affect the total duration of the experiment. Checking fast will mean fewer cycles at each frequency (and higher noise) which means shorter total time. It is possible to edit the script forcing the system to minimize the number of cycles run at each frequency, though that can lead to bad data if one is not careful. Another way to speed up EIS experiments is to use multi-sine, which will be covered in more detail shortly. One final possibility is, unfortunately, if a sample is not stable enough, that the lowest frequency data must be cut. This is unfortunate because low frequency data tends to be more information rich for EIS. If a sample just isn't stable enough to get a result, and can't be made in such a way as to get access to it, then the researcher is going to have to deal with not having that information or try and find another way to get at it. There's only so much that can be done, though knowing that stability does not allow for a measurement to take place can still be useful information.

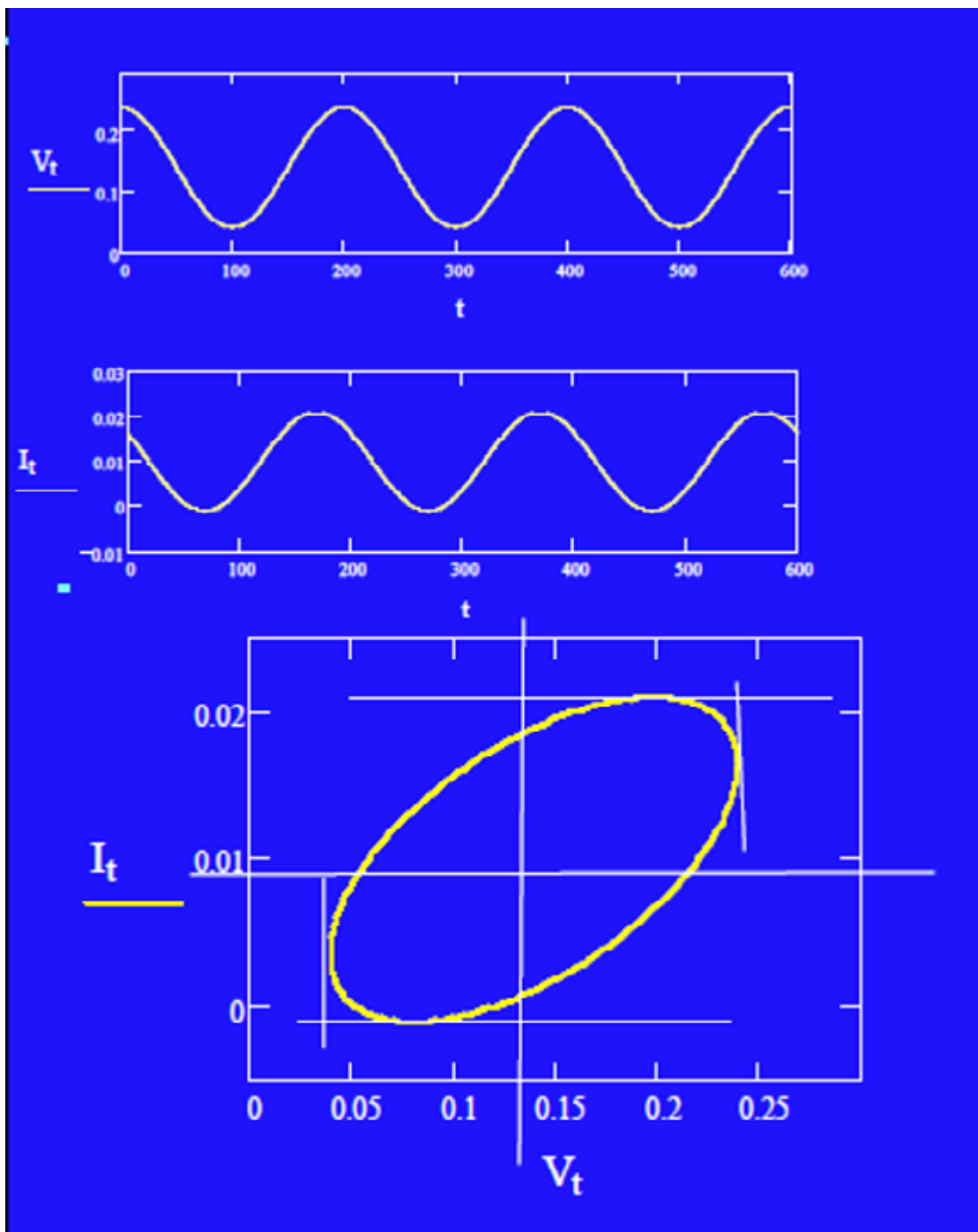


Figure20: Single sine EIS in time domain and as a Lissajous.

In terms of speeding up an EIS experiment, it is helpful to know how EIS works. Fundamentally to do EIS a sine wave is applied, and its response measured. The signal and response are plotted and fit to extract the impedance as well as DC offsets. That single sine experiment is repeated across a range of frequencies, with each frequency done discretely.

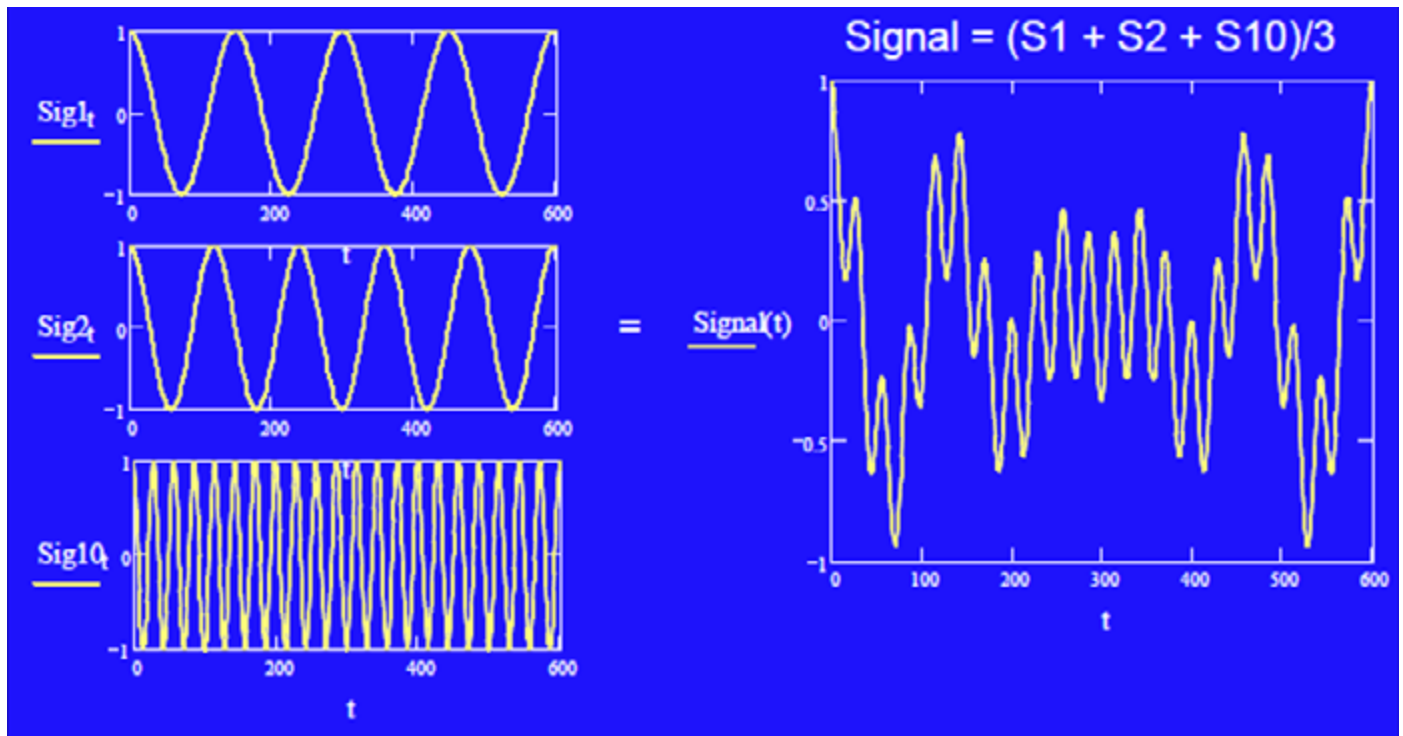


Figure 21: Multisine: three distinct frequencies (left) are summed to create a multi-sine signal (right)

Thanks to the nature of EIS it is possible to apply multiple frequencies concurrently and use Fourier transform to disentangle them at the end. Figure 21 shows an example of three different frequencies summed together. Looking at 3 distinct frequencies is easier to understand but it doesn't speed the EIS collection much so it's better to go further. Figure 22 shows a 24 frequency set.

$$S[i] = \sum_{k=0}^{K-1} A_k \cdot \cos(2\pi(f_k \tau i + \varphi_k))$$

A 's are a unity
 φ 's are random

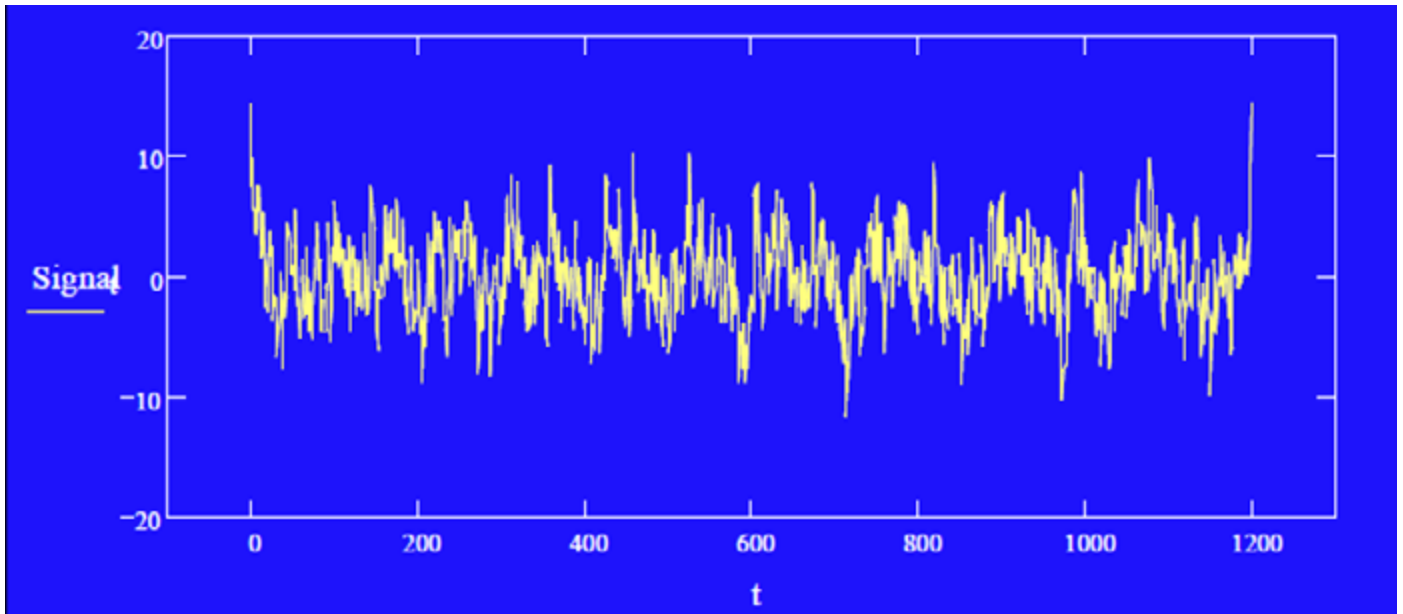


Figure 22: Multi-sine signal with 24 frequencies spanning 2 decades of frequency bandwidth.

The signal in Figure 22 looks a lot like noise to our eyes, but thanks to Fourier transforms, that signal can be deconvoluted to get the actual independent frequency data back out of it. The Gamry version of multi-sine does a couple of additional steps following that. The signal in Figure 22 has the same amplitude for each frequency and the phase shifts are randomized. Adjusting the phases deliberately can reduce the total signal amplitude (too much amplitude can mean a non-linear response, but too little means the final signal/noise may be too low). A second step is an amplitude optimization. When applying a multi-sine signal the higher frequencies are going to have a larger total number of cycles than low frequencies, because of that it is possible to use smaller relative amplitudes for the high frequencies and larger amplitudes for the low frequencies to improve the signal-to-noise ratio. Figure 23 shows the actual signal after phase and amplitude adjustments have been applied.

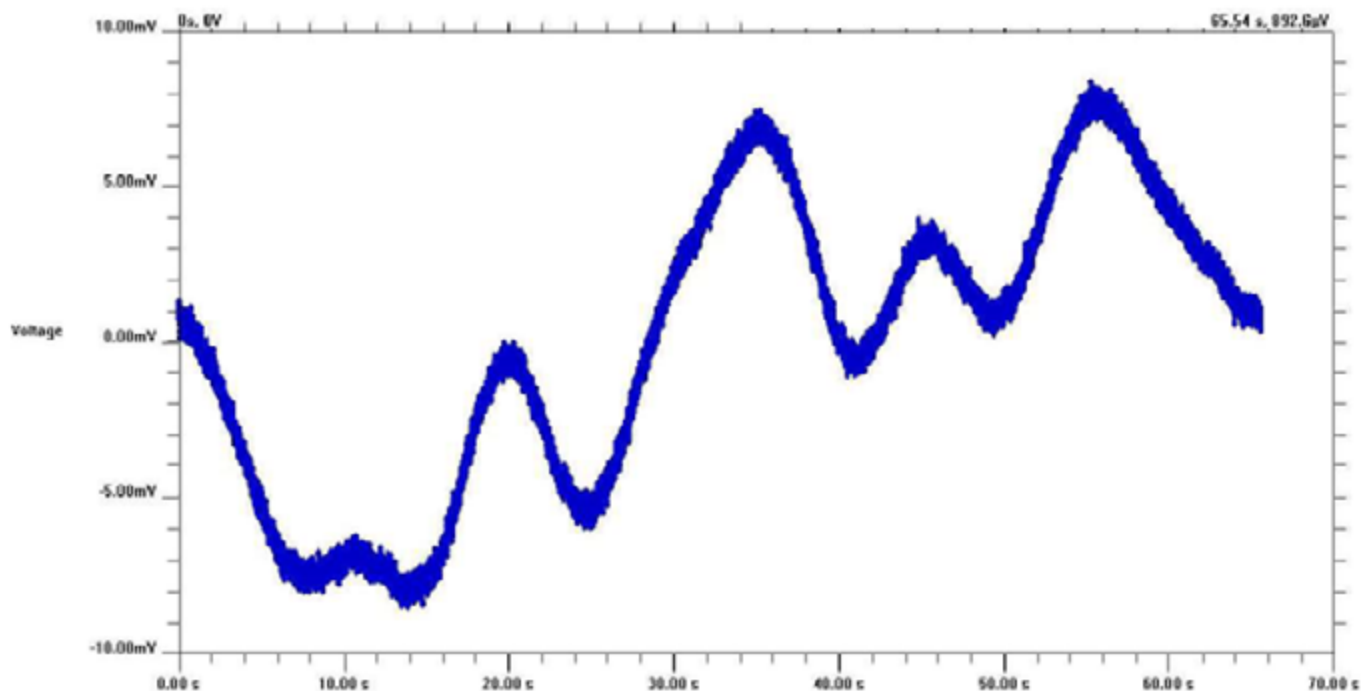


Figure 23: *Multi-sine signal after optimization*

That signal still doesn't look like much but, again, because it can be deconvoluted, quality impedance data can be obtained—see Figure 24 for multi-sine vs. single sine EIS data. Because so many frequencies are being applied and measured simultaneously, the total time for the experiment can be reduced significantly.

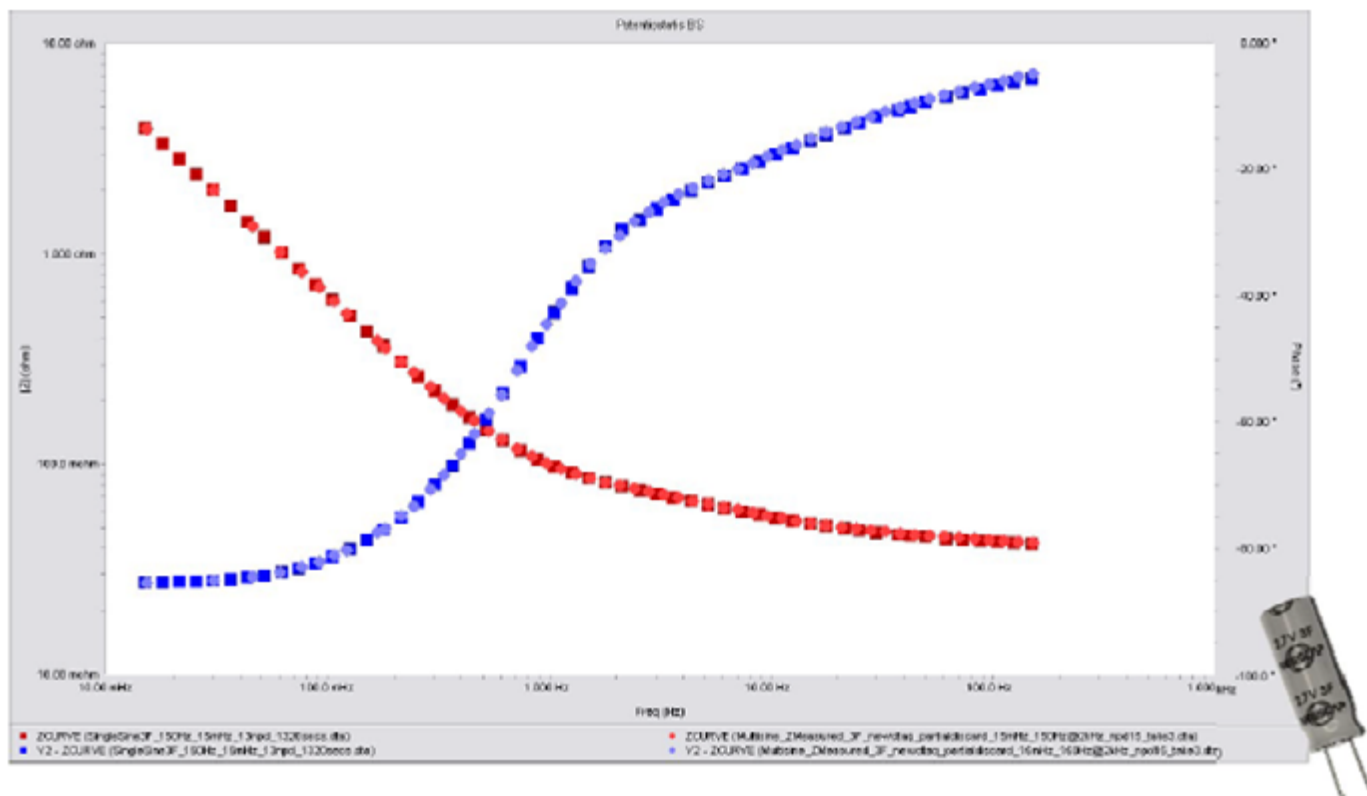


Figure 24: Comparison of single and multiple sine EIS spectra for a 3 F capacitor

Multi-sine EIS isn't perfect and it can't speed the experiment up by orders of magnitude. Still, because the low frequency dominates the total time it takes to make EIS measurements by measuring as many frequencies as possible in the time it takes to measure the lowest frequency being applied, one can get the results significantly faster than if run a signal frequency at a time. The improvement in total time is, roughly, a factor of four.

Naturally there are many more difficult samples than just those addressed above. There are some samples that are simply hard to use with conventional cells. In those cases, creativity is often in order. Control over the active area and edge effects and other aspects is necessary to get the best, understandable results. This may require the use of setups other than conventional three-electrode cells. Figure 25 shows an example of testing a piece of steel. The sample has a curved surface which doesn't mount very well. It also has edges that should not be wetted because they have a different behavior than the plane. Above the sample is a graphite rod wrapped in a paper towel soaked in electrolyte that is making contact to the sample.

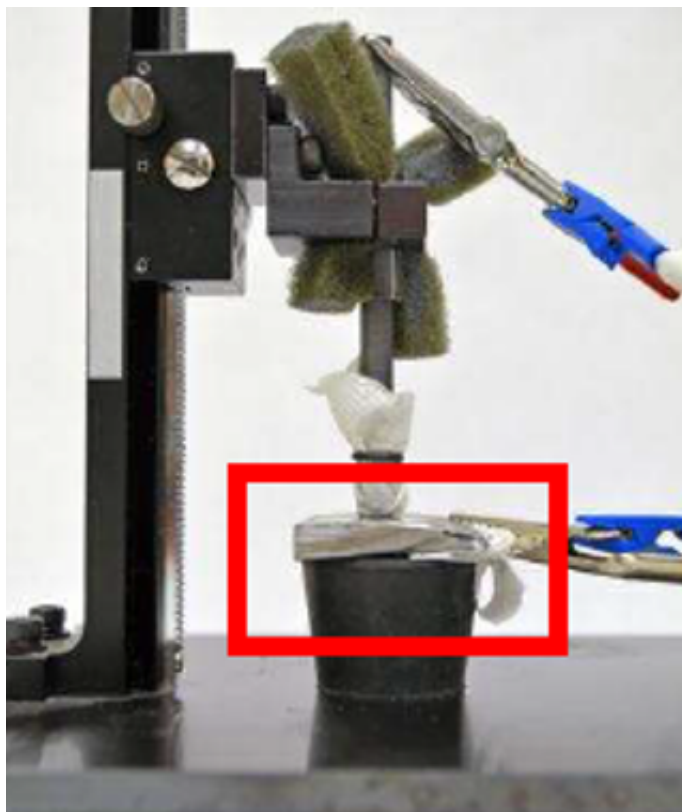


Figure 25: *A difficult curved sample*

The wetted surface is restricted to just the diameter of the graphite rod. This means the area is known—the area of the graphite rod—and a two-electrode measurement can be run on this setup to get data. More details of this particular setup can be found on the application note: EIS on Curved Electrodes (<https://www.gamry.com/application-notes/EIS/eis-on-curved-electrodes/>).

To conclude: when it comes to difficult samples and systems, connections matter; cable layout matters. A Faraday cage should be used for high impedance and low current experiments. The reference electrode is a critical, often overlooked, component. Grounding should be managed properly. Finally, think about cell setup. If something isn't working, then the setup may need to be changed. Sometimes there are people doing similar work, who can be asked for advice. Sometimes something quite different is being attempted, and it will be necessary to figure it out. Creativity in trying to figure out how to actually get samples to be measurable is part of the scientific process.

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- Boostable to 30A



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- EIS included



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- Temperature monitoring
- EIS included (20 kHz)



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