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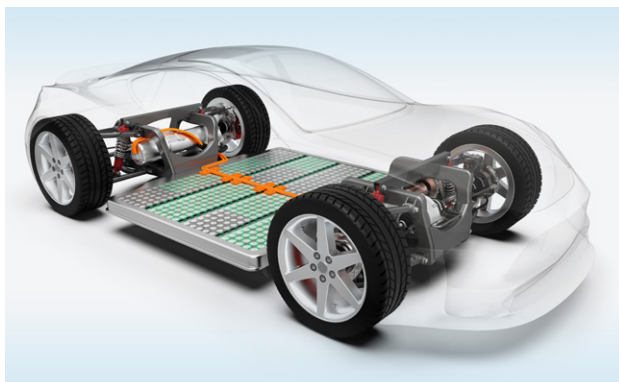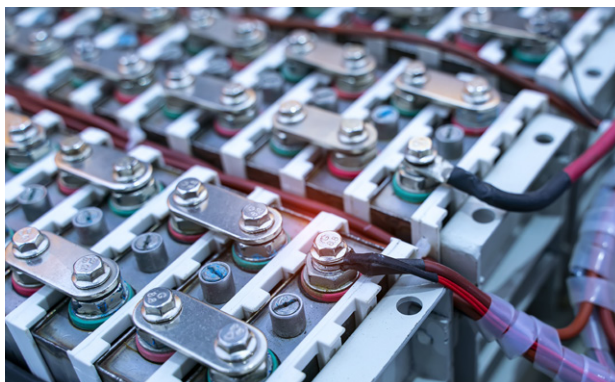
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ELECTROCHEMICAL IMPEDANCE
SPECTROSCOPY (EIS) –
A POWERFUL ELECTROCHEMICAL TECHNIQUE

GAMRY
INSTRUMENTS

COMPETENCE
CREATES
CONFIDENCE

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II.   INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a powerful electrochemical technique that has enjoyed wide acceptance in the modern electrochemical laboratory. EIS is routinely used in battery development, sensor evaluation, fuel cell characterization, corrosion science, and paint testing. Wherever the focus of investigation is, the electrochemical double layer on a heterogeneous interface between a solid electrode and an electrolyte or a working- and counter electrode at the same time in perspective to an embedded reference electrode, EIS offers a powerful tool.

The EIS experiment places some critical demands upon potentiostat performance. Gamry understands to handle the sometimes-subtle potentiostat behavior and how it is affected by the sample. More than anyone, Gamry designs potentiostats for EIS and therefore every Gamry potentiostat leaves the factory ready to perform EIS.

In 1995, Gamry pioneered a novel-single-sine EIS technique called Sub-Harmonic Sampling. Every Gamry Potentiostat includes electronics for Sub-Harmonic Sampling, so there's no need to purchase any additional instrumentation.

Several benefits derive from Sub-Harmonic Sampling enabled instruments:

- Accuracy and precision are equal to or better than other EIS techniques

- The instrument footprint is small, saving bench space

- The instrument configuration is simplified – no tangled mess of BNC cables connecting several instruments

- The ability to tailor the Gamry EIS System to your specific sample is not compromised

- Lower costs than alternative techniques

If a special application arises, Gamry's Open Source Scripting allows to make software changes on your own to perform custom experiments either in the data acquisition or the data analysis. If needed, Gamry can modify the software to match specific necessities. A Sequence Wizard can be used to combine EIS measurements with other electrochemical techniques to create a user defined experiment in an automated order.

Another step forward to enable even more automation is provided by Gamry's Electrochemistry Toolkit that allows users to create custom experiments and OEM companies are able to integrate potentiostats into their own systems using their own software for control. In general if you are looking for the most flexible system for controlling a potentiostat, the Echem Toolkit is the best solution allowing complete customization.

The Gamry Electrochemistry Toolkit comes with ready to use examples for LabVIEW, Python, Visual Basic for Applications utilizing Microsoft Excel, and C++. These examples, combined with the html reference manual provide a firm ground to begin with. Or you simply call a function from your third party software interface to start your own customized experiment and sequence respectively within the straight-forward Gamry Framework Software.

III. AC CIRCUIT THEORY AND REPRESENTATION OF COMPLEX IMPEDANCE VALUES

Almost everyone knows about the concept of electrical resistance. It is the ability of a circuit element to resist the flow of electrical current. Ohm's law defines resistance in terms of the ratio between voltage E and current I.

$$R = \frac{E}{I}$$

While this is a well-known relationship, it's use is limited to only one circuit element – the ideal resistor. An ideal resistor has several simplifying properties:

- It follows Ohm's Law at all current and voltage levels.

- Its resistance value is independent of frequency.

- AC current and voltage signals through a resistor are in phase with each other.

The real world contains circuit elements that exhibit much more complex behavior. These elements force us to abandon the simple concept of resistance. In its place we use impedance, which is a more general circuit parameter. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current. Unlike resistance, impedance is not limited by the simplifying properties listed above.

Electrochemical impedance is usually measured by applying an AC potential to an electro-chemical cell and measuring the current through the cell. Suppose that we apply a sinusoidal potential excitation. The response to this potential is an AC current signal, containing the excitation frequency and it's harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series).

Electrochemical Impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase.
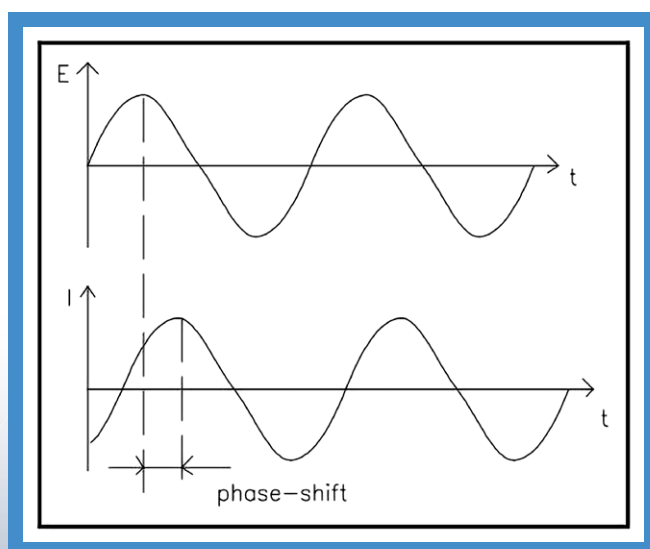
Figure 1:
Sinusoidal current response in a linear system

The excitation signal, expressed as a function of time, has the form

$$E_t = E_0 \cdot \sin(\omega \cdot t)$$

E(t) is the potential at the time t, E_0 is the amplitude of the signal, and ω is the radial frequency. The relationship between radial frequency ω (expressed in radians per second) and frequency f (expressed in hertz / Hz) is:

$$\omega = 2 \cdot \pi \cdot f$$

In a linear system, the response signal, I(t) is shifted in phase (ϕ) and has a different amplitude, I_0

$$I(t) = I_0 \cos(\omega \cdot t - \text{Ø})$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z = \frac{E(t)}{I(t)} = \frac{(E_0 \cdot \cos(\omega \cdot t)}{I_0 \cdot \cos(\omega \cdot t - \text{Ø})}$$

The impedance is therefore expressed in terms of magnitude, Z_0, and a phase shift, ϕ.

If we plot the potentiostatically applied sinusoidal signal on the X-axis of a graph and the sinusoidal response signal I(t) on the Y-axis, an oval is plotted. This oval is known as „Lissajous figure". Analysis of Lissajous figures on oscilloscope screens was an accepted method of impedance measurement prior to the availability of lock-in amplifiers, frequency response analyzers and digital signal processing.
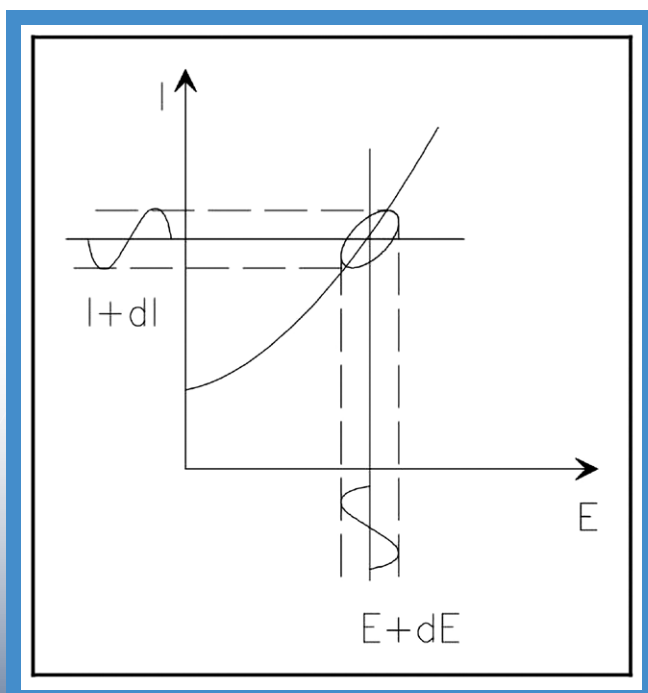

Figure 2:
Origin of Lissajous Figure

IV. EIS WITH DIGITIZED SIGNALS USING „DIRECT DIGITAL SYNTHESIS (DDS) AND SUB-HARMONIC SAMPLING"

Gamry has approached precise electrochemical impedance measurements using Sub-Harmonic Sampling and Direct Digital Synthesis to allow EIS measurements to frequencies as high as 1 MHz and more with no further external device such as a Frequency Response Analyzer (FRA).

DDS employs digital signal processing techniques to generate a true sine wave at the desired frequency and synchronizes it very precisely to the Potentiostat's data acquisition time base.

Current and voltage waveforms recorded at higher excitation frequencies must be transformed to lower frequencies prior to analysis. Sub-Harmonic Sampling solves this by using the Analog/Digital Converter to sample either current and voltage correctly. The A/D's data acquisition frequency is chosen to take samples at different points on different cycles of the AC waveform (see Figure 3).
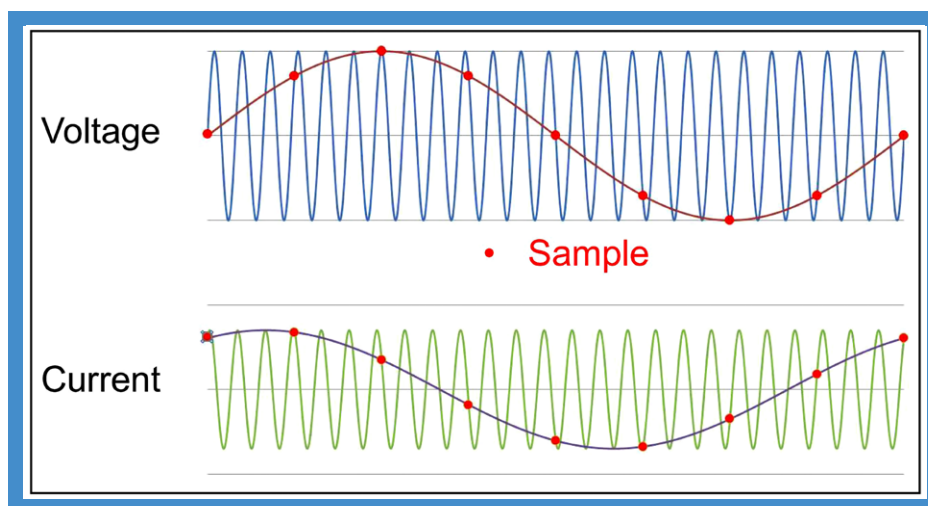

Figure 3:
Sub Harmonic Sampling of Voltage and Current Waveforms (the green trace is the AC signal from the sample. Sampling the sub-harmonic data points (•) give AC current and voltage results incl. correct phase-angle information.

At 100 kHz, for example, the system takes data on every 100th cycle of the current and voltage waveforms using a phase increment in between data points. From this data, amplitude and phase information can be precisely derived. High accuracy is achieved due to DDS and data acquisition clocks are both synchronized with the same crystal oscillator.

Afterwards sampling both curves, they are each transformed into the frequency domain using a discrete Fourier Transform (DFT). Similar calculation of the DC component and subtraction from the AC component provides a measure of noise. Several cycles of data acquisition are averaged to reduce noise to an acceptable level.

Using Ohm's Law results in the complex quantity of Z which is plotted either as $Z_{magnitude}$ and Z_{phase} vs. Frequency in a Bode plot or as $Z_{imaginary}$ vs. Z_{real} in a Nyquist plot.

Several correction factors are applied to Z either by post-production calibration or by the regular AC calibration routine. They consist of corrections for reproducible sample time delays and roll-offs affecting mismatch between I and V channel filters or channel range amps.

V. HIGH FREQUENCY EIS LIMITATIONS DUE TO INSTRUMENT BANDWIDTH

In the past waveform signals were generated with analog methods, for example phase-locked loops (PLL), to create a sine wave. Nowadays, these signals are digitized which means that the requested waveform is approached with a staircase waveform underneath.
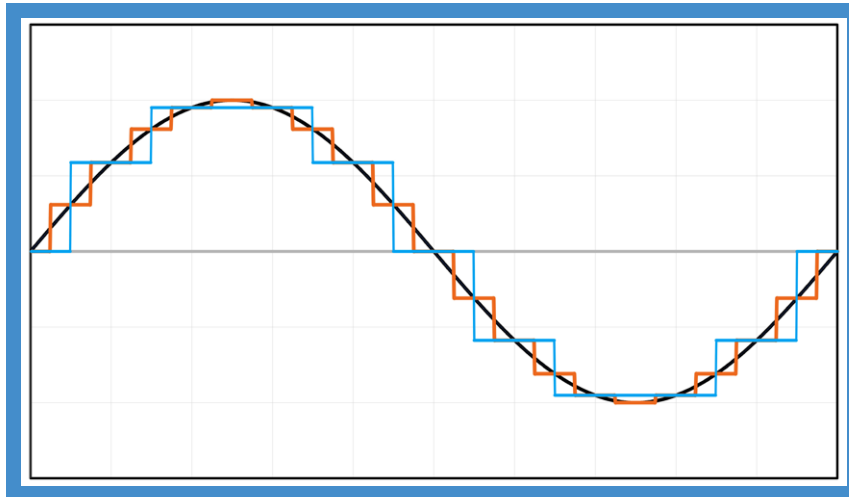

Figure 4:
Graphical representation of a sine wave showing its digitized staircase form using two different resolutions in approximation (coarse / fine)

Width (time scale) and height (amplitude scale) of each signal depend on the sample rate and the magnitude resolution of the instrument. The smaller these steps can be, the better a signal can be simulated.

As sample rate (f_{CLK}) represents the limiting factor for high-frequency signals, it must be at least twice as big as the requested signal frequency = $f_{Nyquist}$ (Nyquist criterion). Therefore, a sine wave can be first reproduced if the sample rate and data acquisition frequency respectively is at least equivalent or even lower than $f_{Nyquist}$ in order to approximate the sine wave even better than necessary.

$$f_{Nyquist} = \frac{1}{2} f_{CLK}$$

However, not only the sample rate and clock frequency respectively is restricting the usable frequency range. High-frequency signals mean also fast signal changes (step height) which need to be processed by the control amplifier. In order to handle those signals, the bandwidth of the control amplifier (CA) needs to be sufficiently high so that signals can be properly adjusted and applied to a cell. Other factors that determine the usable frequency range derive from the measurement setup. Cell cables can have a huge influence on the quality and bandwidth of a signal. Instrumental artifacts such as stray capacitance and inductive effects can drastically limit the frequency range. Therefore, a Gamry Instrument is always designed and optimized for its purpose as one channel in one single chassis.

VI. CABLE CAPACITANCE

The individual conductors in the potentiostat's cell cable are made up of coaxial cables. The outer conductor in a coaxial cable is used to shield the signal of interest. Cable capacitance arises in coaxial cables because of the insulation between the shield and the central wire. It takes a certain amount of time for the cable to reach its charged level. This lag in charging time slows down the signal being transmitted, and even interferes with that signal. This effect is particularly pronounced for high-frequency signals like those that occur in Electrochemical Impedance Spectroscopy (EIS) measurements.

If we consider the example of digital data pulses represented by a square wave with near-vertical rises and falls entering one end of a coaxial cable, a cable with a high capacitance slows these voltage transitions so that they come out of the cable's opposite end looking more like saw-teeth (see Fig. 5). The end result is a distortion of the signal – and your data.
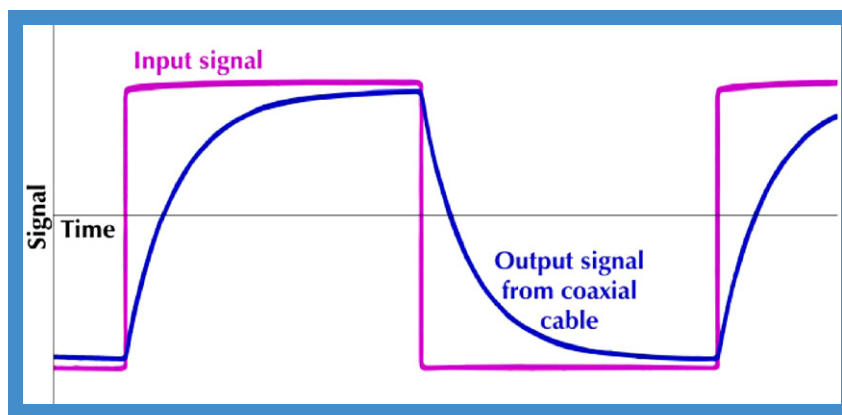
Figure 5:
Example of a Square Wave Signal (purple) passed through a coaxial cable (blue)

A lot of research goes into minimizing the cable capacitance. Some ways to accomplish this include increasing the wall thickness of the insulation, decreasing the conductor diameter, or using insulation with a lower dielectric constant. Another way to handle this problem is via software correction.

For cable capacitance correction, you would want to apply the second level of correction, where tiny differences caused by the manufacturing process of the cell cable appear as residual error of approx. 1 % afterwards 99 % of error have already been removed with factory calibration using a standard cable.

Removal of this residual error plays an important role whenever the cell cable capacitance dominates the measurement or in other words, when you switch from a 10 nF capacitor measurement without any phase glitches to a 470 pF capacitor measurement incl. inaccurate phase angle information during „Auto-Ranging" when cable capacitance calibration was not taken into account in advance!

Remember, cable-capacitance correction is most useful on high-impedance, low-capacitance cells. Cable-capacitance correction is not useful for devices with lower impedances such as batteries, supercapacitors, and fuel cells where mutual inductance among others is the limiting factor for low impedance high frequency EIS data acquisition.

VII. MUTUAL INDUCTANCE DURING EIS MEASUREMENTS OF SMALL IMPEDANCES

A "mutual inductive" effect limits the ability of any system to measure small impedances at higher frequencies. 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 windings of a transformer, and the sense leads are the secondary windings. The AC current in the primary creates a magnetic field that then couples to the secondary, where it creates an AC voltage.

You can minimize the unwanted effect in a number of ways:

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

A   Avoid higher frequencies

Mutual inductance is an inductive effect. The voltage error is given by:

$$V_s = M \cdot \frac{di}{dt}$$

where V_s is the induced voltage on the secondary, M is the coupling constant (with units of Henries), and di/dt is the rate of change in the primary current. M depends on the closeness of the coupling and can range from zero up to the value of the primary inductance (the inductance in the current-carrying leads).

Assuming a constant-amplitude waveform in the primary, di/dt is proportional to frequency. There is always a frequency below which the effect of mutual inductance errors is unimportant. Unfortunately, many electrochemical systems need information at frequencies above this limit.

B   Minimize the Net Magnetic Field

A current passing through a wire creates a magnetic field. The field strength is proportional to the current. Fortunately, passing the same current in opposite directions through adjacent wires tends to cancel the external field. This also minimizes the net inductance in the wires.

From basic physics, the E x B cross-product relationship for current through a wire obeys the Right-Hand-Rule: if your right thumb points in the direction of the current flow in a wire, when you curl your fingers around the wire, the magnetic field curves around the wire in the same direction as your fingers. The current in the primary wires is flowing in opposite directions in the two wires of the cable, so your thumb points in opposite directions for each wire, causing some cancellation of the fields. If the wires were superimposed, in exactly the same place, the cancellation would be perfect.

Because the wires cannot be in identically the same location, the cancellation is imperfect, and some net magnetic field is always present. The more the wires are separated, the larger the net field.

The most common arrangement for inductance and field minimization is the twisted pair. Two insulated wires are simply twisted together. A coaxial-wire arrangement with current flowing in opposite directions in the center conductor and the outer conductor is also effective.

C Separate the pairs

If you place a magnetic-field probe near a wire passing current, you measure a field inversely proportional to the square of the distance between the probe and the wire.

In an electrochemical system, the probe is our sense wiring. Separating the sense wires from the current-carrying wires can dramatically reduce the magnetic coupling, reducing errors in the EIS measurement.

Reference 3000 and Interface 5000 have two cell cables, so that we can separate the current-carrying wires from the sense wires. The current-carrying pair is in the Counter/Working Cable and the sense pair is in the Sense Cable.

D Twist the Sense Wires

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

Twisting the sense wires together helps in two ways, even though twisting the wire forms loops:
- The twisted wires are forced to lie close to each other, minimizing the loop areas.
- Adjacent loops pickup voltages of opposite polarity, resulting in cancellation.

E How Should You Hook Up Your Cell?

Always use four-terminal connections to the cell. Try to avoid conductors that are shared by both the current-carrying path and the voltage-sensing path.

If your experiments are in the region where mutual inductance may limit performance, keep the voltage-sensing leads in a twisted pair and the current-carrying leads in a different twisted pair. Keep the pair of sensing wires far away from the pair of current-carrying wires. Try to arrange each pair so that they approach the cell from opposite directions.

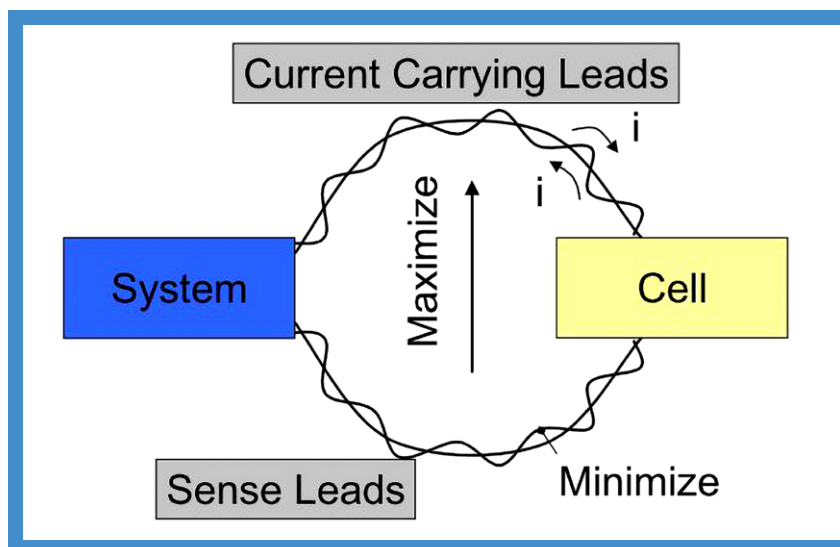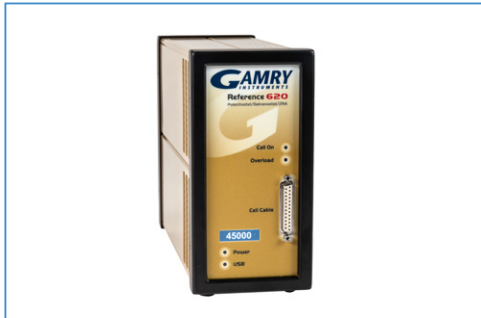These recommendations are summarized in the Figure below.

Figure 6:
Wiring Recommendations

VIII. EXAMPLES OF INSTRUMENTS AVAILABLE

A   Reference Line of Instruments:

Reference 620

- Designed for fast, low-current measurements
- Fast CV
- High speed pulsing and sampling
- 11 V, 600 mA
- EIS to 5 MHz

Reference 3000

- Perfect for high and low current applications
- 32 V / 1.5A and 15 V / 3 A
- EIS to 1 MHz
- Boostable to 30A @ +20V/−2.5V

Reference 3000AE

- Additional voltage measurements for stacks and ancillary devices
- Perfect for high and low current applications
- 32 V / 1.5A and 15 V / 3 A
- EIS to 1 MHz
- Boostable to 30A @ +20V/−2.5V

Interface 1010E

- General purpose
- Great for most applications except insulating coatings
- 12 V, 1 A
- EIS to 2 MHz

Interface 1010B

- The perfect introductory instrument for physical and analytical electrochemistry applications
- 12 V, 1 A

Interface 5000E

- High current testing of single cell energy devices
- Second voltage measurement for simultaneous anode and cathode measurements
- Temperature monitoring
- 6 V, 5 A
- EIS included

Interface 5000P

- Great introductory 5 A instrument designed for testing of batteries, supercapacitors and fuel cells
- 6 V, 5 A
- Dual voltage measurements
- Temperature monitoring
- EIS included (20 kHz)

Multichannel

LPI

Reference 3000 with Booster