ApplicationNOTE

GAMRY INSTRUMENTS

EIS Measurement of a Very Low Impedance Lithium Ion Battery

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 useful 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 cannot be easily or accurately measured using laboratory EIS systems. Most commercial EIS system do not work well when impedance is below 0.1 Ω.

This Application Note describes a series of EIS measurements made on a Li ion secondary battery rated to have impedance below 500 μΩ at 1 kHz. Special techniques are used to improve the accuracy and frequency range of this difficult measurement.

If you're new to EIS, you might want to read Gamry Instruments' **Basics of EIS** before reading the rest of this Application 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.

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 pick up 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.

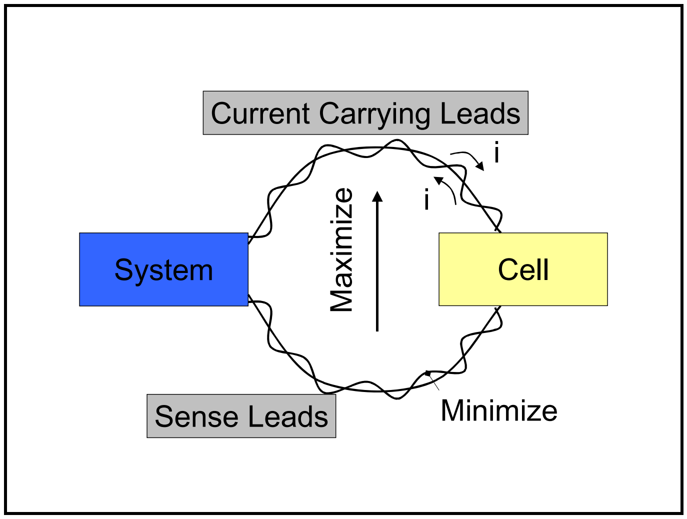

Figure 1. Recommended Cell Connections.

Mutual inductance errors are more significant with 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 special twisted-pair cables for our EIS systems. The results below show how one of these cables improves the measured EIS spectrum of a battery.

Special Techniques

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 connection fixture.
- Use a low impedance cell surrogate to measure residual cable 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 be used to illustrate the importance of these guidelines.

Experimental

The Battery

Lithium Technology Corporation donated the Li ion battery used in these tests. Its data sheet refers to it as GAIA 45 Ah HP-602050. It is a large cylinder – about 60 mm in diameter and 230 mm long – with a threaded terminal at either end.

This battery was designed for use in high rate applications including electric automobiles. Its "AC impedance" is specified as less than 500 μΩ at 1 kHz. The open circuit potential of the battery was measured before each test. The reading was always 3.716 volts. This voltage indicates an intermediate state of charge.

Electronics and Software

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 supplied with the Reference 600.

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.

The battery's connections to the EIS system are described in a later section of this note.

Battery Surrogate

A battery surrogate was built to have the same geometry and to connect to the EIS system in the same way as the battery.

A 204 mm long cylinder was cut from a 64.5 mm diameter round aluminum (alloy 2011) bar. A 15 mm deep, 10.2 mm diameter hole was drilled into each end of this aluminum cylinder. These holes were hand tapped to accept a metric 12mm x 1.75 thread.

Two 25 mm long pieces of brass-threaded rod were screwed into the threaded holes to mimic the battery terminals. A 24 mm OD, 2.5 mm thick copper washer was added to each terminal. It spaced the contact above the Al cylinder. With these washers in place the battery surrogate had a connection-to-connection length roughly the same as that of the battery.

An overall covering of 63-micron mylar packing tape was used to insulate the aluminum body of the surrogate. This covering prevents unwanted connections between the fixture and the battery surrogate. The only contact should be at the terminals.

The Connection Fixture

The connection fixture was built from 1.6 mm thick copper sheet. Two strips, 25 mm wide and 250 mm long were cut from the sheet.

A 12.7 mm diameter round hole was drilled in the center of each strip. The area around the hole was smoothed using a file followed by 150-grit sandpaper. Four stainless steel captive nuts were pressed into the end of the strips. A brass screw in each nut formed a contact point. The bare wires in Gamry's Low Impedance Cell cable were compressed in each contact point.

The strips were bent at right angles to fit over the Lithium Technology battery. Brass nuts were used to firmly connect the fixture to the battery.

CAUTION: If the two strips in the battery connection fixture ever come into electrical contact while the battery is connected, a current of thousands of amperes will flow. This may harm the battery, the fixture, or even the experimenter. Be very careful to avoid this situation.

Figure 2 is a photograph of the battery in the fixture and the battery surrogate. The current carrying wires are on one side of the battery and the sense wires are on the other. The wires in the Low Impedance Cell cable are kept twisted as long as possible before they split to connect to the fixture.

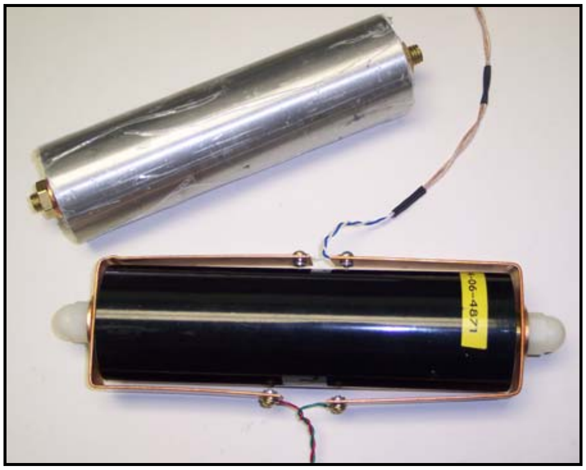

Figure 2. Battery in Fixture and Surrogate.

Why Galvanostatic Mode?

Current, voltage, and impedance are related through Ohm's Law. A voltage of 1 mV across 100 μΩ of impedance corresponds to 10 A.

No commercial potentiostat is specified to control a typical battery potential (>1.2 volts) with < 1 mV of error. When a potential with a > 1 mV error is applied to a low impedance battery a very large DC current will flow.

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. A modern EIS system with AC coupling or offset and gain in the voltage measurement can measure of microvolts of AC voltage superimposed on the DC battery voltage, which is typically very stable.

Why Use Large Excitation Currents?

The voltage signal in a galvanostatic EIS experiment 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 at least 10 μV. For a 100 μΩ cell, this means the current must be >100 mA.

Why Use Twisted Pair Wiring and a Connection Fixture?

Figure 3 shows the importance of wiring in EIS measurement of a low impedance battery. There are 3 Bode plots overlaid in this graph. In all the plots, the dark colors are magnitude and the corresponding light colors are phase. All curves were recorded on the Lithium Technology battery described above.

The black and grey data were recorded using the Reference 600's standard cell cable with alligator clips. 18 AWG tinned copper wire squeezed between washers on the battery terminals was used as an attachment point for the alligator clips.

The red and pink data were recorded with Gamry's Low Impedance cable for the Reference 600. The tinned copper wires on this cable were squeezed between copper washers on the battery terminals.

The dark and light blue data were recorded using the battery held in the battery fixture. The wires on the Low Impedance cable were only untwisted for about 2 cm before they were connected to the fixture. See Figure 2.

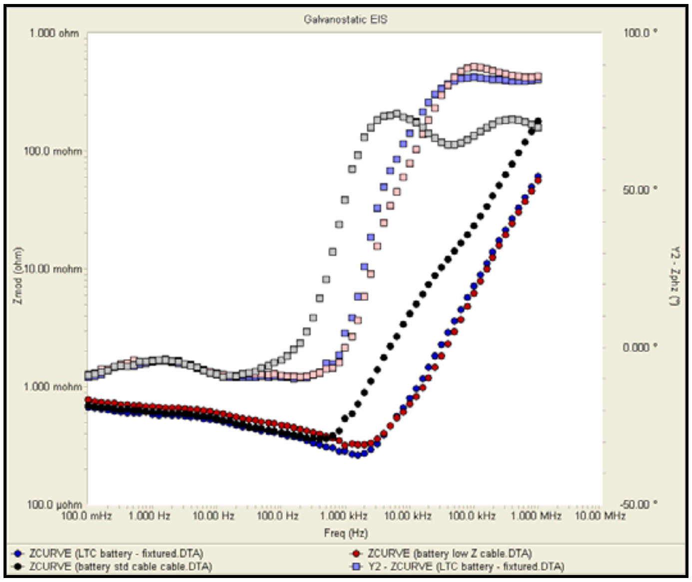

Figure 3. Battery Spectra with Various Connection Schemes.

All the curves have the same basic shape, but the impedance becomes lower as the connections are improved. Notice the difference between the red and blue curves at frequencies between 1 kHz and 3 kHz. The impedance with the fixture is about 20% lower than the impedance with the cable alone.

If the high frequency data is fit to an inductor model, the calculated inductance is 38 nH with the standard cable and 11 nH with the Low Impedance Cable.
A detailed discussion of the shape of the battery's spectrum will be deferred to the end of this document.

How is the Battery Surrogate Used?

The previous graph and discussion showed the importance of cabling on the measurement. But, even for the best curve, one doesn't know how much of the measured impedance is the true battery impedance and how much to attribute to residual cabling effects.

A battery surrogate allows you to measure the cabling effects. The surrogate is a metal object with the same geometry and connection scheme as the battery. It should be built to have as little resistance and inductance as possible.
The resistance of the aluminum and brass surrogate described can be estimated from the bulk resistivity of the materials used in its construction. The estimated resistance is less than 10 µΩ. The measured resistance was higher because the machining on the aluminum rod was done by hand and thus imperfect -- the washers used to make contact to the connection fixture had small gaps between them.

The spectrum of the surrogate was recorded using the same wiring and experimental conditions as the battery test. Figure 4 shows Bode plots of the surrogate (red points) and battery spectra (blue points) recorded using the connection fixture.

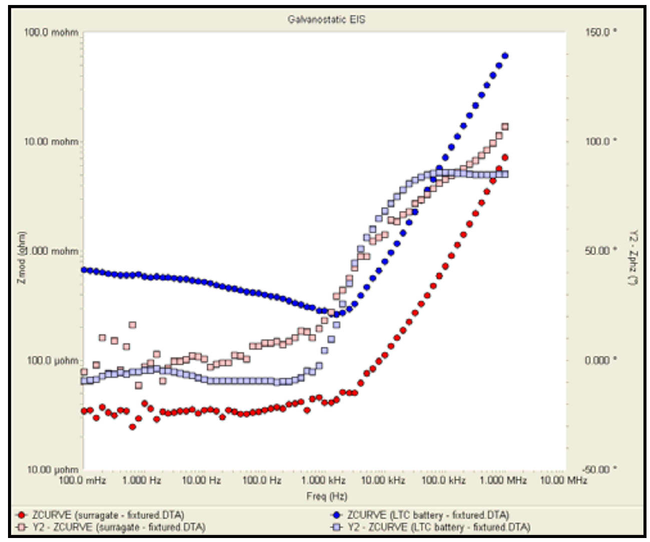

Figure 4. Battery and Surrogate Spectra.

The surrogate spectrum is resistive at low frequencies and becomes inductive at higher frequencies. A series RL model fits well to this spectrum, yielding an R value of 34 µΩ and an L value 1.3 nH.

Is Spectrum Subtraction Useful?

Resistive and inductive errors caused by imperfect cabling and connections both result in impedance in series with the cell's true impedance. A series subtraction of the surrogate's spectrum from the battery's spectrum can remove these effects.

Figure 4 showed that the impedance of the surrogate is at least one decade smaller than that of the battery at all frequencies.

A Bode plot of the battery's spectrum before (red points) and after subtraction of the surrogate's spectrum (blue points) is shown in Figure 5.
As expected, the subtraction had little effect. Cabling common to both battery and surrogate does not cause the inductance above 1 kHz, so subtraction of the surrogate's spectrum does not change the curve in this region. The decrease in impedance near 1 kHz may not be desired – it may be the result of the non-ideal, non-zero resistance of the surrogate.

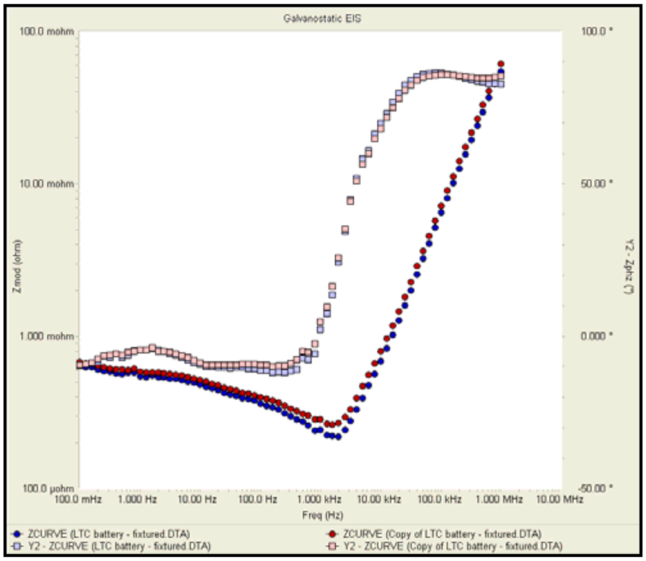

Figure 5. Corrected and Uncorrected Battery Spectra.

Correction by spectrum subtraction is not warranted in this system. It has proven useful in other systems where cabling creates more significant errors.

What Does the Spectrum Tell Us?

Look back at the uncorrected spectrum in Figure 5. A Kramers-Kronig (K-K) fit of the spectrum (not shown on this plot) shows no signs of measurement non-linearity.
The battery's impedance at 1 kHz (280 µΩ) is well below the battery's 500 µΩ specification. This test, at room temperature and one battery potential, does not guarantee low impedance at other states of charge or temperatures.

Above 1 kHz, the impedance of the battery increases by a decade for every decade in frequency and the phase shift approaches 90°. This behavior is typical of an inductor. Correction of the battery's spectrum by subtraction of the surrogate's spectrum did not alter this behavior, leading to the conclusion that the battery itself is inductive. A fit of the uncorrected impedance between 5 kHz and 500 kHz to an inductor model gives an L value of 11 nH.

At lower frequencies, between 0.1 Hz to 1 kHz, the battery's impedance falls as frequency increases while the phase stays between -5° and –25°. This behavior seems unusual, at least in terms of the standard electrical elements used to model impedance. The most probably explanation for this unusual behavior is a distribution of parameters in a multitude of more traditional equivalent circuit elements. The distribution may be over a range of particle sizes, pore sizes, distances, or even reaction rate constants.

Tests at Low Frequencies

Figure 6 shows the Bode plot of the battery's spectrum extended to 600 µHz. These data were measured more than a year later than the data above.

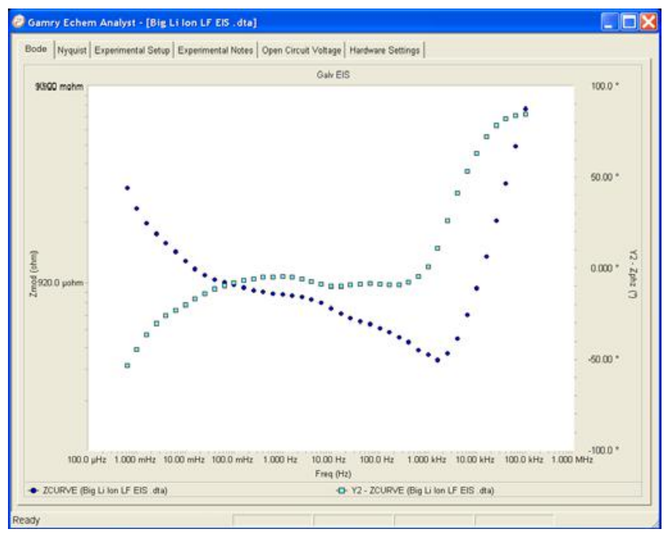

Figure 6. Extending the Spectrum to Lower Frequencies.

An equivalent circuit model for the EIS behavior of a battery generally includes a double layer capacitance element and a polarization resistance element.

At frequencies below 10 mHz, the measured impedance rises as the frequency gets smaller and the phase heads toward -90˚. This behavior is indicative of a capacitor in parallel with the other cell impedances. This capacitor will probably model as the double layer capacitance of the electrode/electrolyte interfaces. Again, we suspect that the capacitor will not be ideal, but instead show a distribution of elements.

Even at the lowest measured frequency of 600 μHz, there is no evidence pointing to the need for a polarization resistance element in the EIS model. At lower frequencies, its effects may appear in the spectrum, but the measurement time becomes a problem at these low frequencies.

Conclusions

In this Application Note, Gamry Instruments presents a number of guidelines for accurate EIS measurements on low impedance cells. Galvanostatic cell control, a large AC current, and reproducible 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 large Li Ion battery.

Impedance measured on the battery is always significantly higher than the impedance of a low resistance metal battery surrogate connected in the same manner as the battery. This implies that the battery spectrum is free from experimental error due to resistance or inductance.

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